A G.C./M.S. Study of the Reaction and Decomposition Products of Pentafluorophenyl-Grignard and Lithium Reagents

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Master of Science

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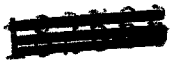

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ABSTRACT

Decomposition and side reactions of, and the synthetic use of, pentafluorophenylmagnesium bromide and pentafluorophenyllithium have been investigated using G.C./M.S. techniques. Their reactions with reagents such as C_6F_5X (X = H, F, Cl, Br, I), $C_6F_4X_2$ (X = H, Cl), $C_6F_3Cl_3$, C_6H_6, $(C_6X_5)_3P$ (X = H, F), $(C_6X_5)_3P{=}O$ (X = H, F), $(C_6X_5)Si(CH_3)_3$ (X = H, F) and $(CH_3)_{4-n}SiCl_n$, n = 1,2, in ether or ether/n-hexane were studied.

In addition to the principal reaction of synthetic use, namely the replacement of a halogen by a pentafluorophenyl group, two types of side reactions were observed. These were (i) intermolecular loss of LiF via a nucleophilic substitution, and (ii) intramolecular loss of LiF, followed by the addition of either inorganic salts such as lithium or magnesium halides, or organometal compounds such as organolithium or organo-Grignard.

G.C./M.S. techniques were routinely employed to study complicated reaction mixtures. Although mass spectrometry alone has disadvantages for the identification of isomers, deduction of the most probable pathway often helps overcome this problem.

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INTRODUCTION

1. Reactions of Fluoroaromatic Organometallics

Since the first successful syntheses of the organometallic intermediates pentafluorophenylmagnesium bromide (1, 2) and pentafluorophenyllithium (3) which both are the sources of pentafluorophenyl anion, research interest in preparations via these precursors has been extensive. Attention is most concentrated on the reactions with metal halides and the results have been the subject of several reviews (4, 5). The major reaction type can generally be illustrated as follows:

$$R_mMX_{n-m} + (n-m)C_6F_5M' \longrightarrow R_mM(C_6F_5)_{n-m} + (n-m)M'X$$

where M' is either Li or MgBr; and R is an element or group other than halogen.

The success of such reactions is mainly based on the reactivities of most metal halides.

I. Pentafluorophenylmagnesium Halides vs. Pentafluorophenyllithium

The choice between these two intermediates must be a compromise. Generally speaking, the pentafluorophenylmagnesium halides, which can be directly made from C_6F_5X (X = H, F, Cl, Br, I) with magnesium metal or indirectly by the aid of activating reagents under various solvents (6), offer the advantages of the ease of preparation and the stability at higher temperature. They are, however, less reactive and thus reaction by-products may form at high

temperature. In contrast, pentafluorophenyllithium can be made from C_6F_5X (X = H, Cl, Br, I) by using either direct metalation or metal/halogen (hydrogen) exchange methods (5), and being more reactive, can be used at lower temperature, reducing unwanted by-products.

II. Other Sources of the Pentafluorophenyl Group, $C_6F_5^-$.

A number of pentafluorophenyl organometallics also provide the pentafluorophenyl group with carbanionic character. These reactions make use of the principle that the carbon-metal bonds of most pentafluorophenyl organometallics are very susceptible to the attack of either nucleophiles or electrophiles. So far, except in the study of cleavage reactions of such carbon-metal bonds and in a few cases where preparation via direct use of pentafluorophenyllithium or pentafluorophenylmagnesium bromide is impossible (e.g. reactions in the absence of solvents), the pentafluorophenyl anion produced by this way has lacked value in synthesis.

Another source of the pentafluorophenyl group is the free radical, $C_6F_5\cdot$, which is believed to have electrophilic properties. It can be formed by several methods (7) and does attack reagents with high electron density sites such as benzene (8). There is no doubt that it provides an excellent way for the addition of the pentafluorophenyl group to the hydrocarbons.

The last preparative route introduced is via hexafluorobenzene, a very good precursor for numerous mono-

substituted pentafluorobenzenes (7), and to a lesser extent, di-substituted tetrafluorobenzenes (9).

$$Nu^- + C_6F_6 \longrightarrow C_6F_5Nu + F^-$$

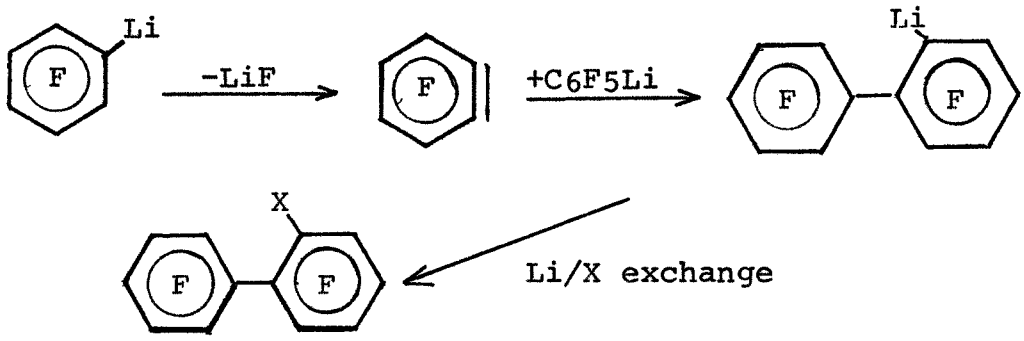
where $Nu^- = H^-, HO^-, HS^-, CH_3^-, CH_3O^-, H_2N^-$, etc.

Since C_6F_6 was commercially attractive at an early stage of the development of aromatic fluorocarbons, its extreme susceptibility to the attack of nucleophiles, resulted in many studies on the nucleophilic substitution of C_6F_6 and its derivatives. Kobrina (9) recently has given a comprehensive review.

III. Reactions of Pentafluorophenyl Anion

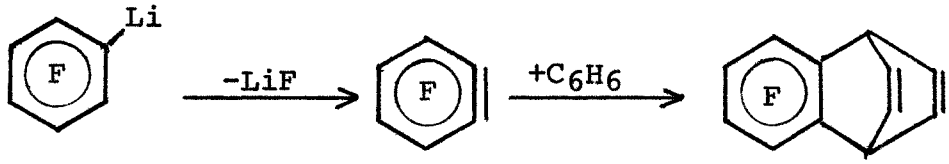
The pentafluorophenyl anion from pentafluorophenyllithium was utilized as a nucleophile at low temperature (below -40°C) as previously illustrated. Its reactions with hexafluorobenzene (10), pentafluorobenzene, bromopentafluorobenzene, and iodopentafluorobenzene (11) have been investigated. The results reported are, small amounts of 4- and/or 2-substitutednonafluorobiphenyls isolated, and unidentified residues. Apparently more vigorous conditions are required and this is usually obtained by raising temperature. In doing so, another pathway competes, namely the intramolecular loss of lithium fluoride which is a common feature of perfluorolithium compound. There is no doubt that the decomposition produces an intermediate, tetrafluorobenzyne, and once it is formed, one molecule of

undecomposed pentafluorophenyllithium can be added to yield 2-lithiononafluorobiphenyl which will further undergo Li/X exchange in the presence of C_6F_5X (X = H, Br, I).



The addition of pentafluorophenyl group to C_6F_5X (X = H, Br, I) via this elimination-addition pathway, in contrast to the nucleophilic substitution by the pentafluorophenyl anion, is easy to carry out and the 2-substitutednonafluorobiphenyl formed is a good starting material for further reaction.

In the presence of chloropentafluorobenzene the decomposition of pentafluorophenyllithium doesn't give 2-chlorononafluorobiphenyl (15), while in benzene the 1,4-addition product is the major product.



This method, on one hand, is used to trap tetrafluorobenzyne thus proving the presence of the benzyne type of intermediate in the course of reaction, and on the other hand

to synthesize new compounds with four fluorines on the benzene ring via Diels-Alder addition.

The further elimination and addition of 2-lithionona-fluorobiphenyl is possible and Cohen et al. (13) demonstrate that at least five elimination-additions have occurred.

IV. Nucleophilic Substitution of Pentafluorophenyl Mercury, Phosphorus and Silicon Compounds

Although pentafluorophenyl organometallics may be regarded as mono-substituted derivatives of hexafluorobenzene, we would like to separate them from others mainly due to d orbital-containing elements involved. Their reactions with nucleophiles are thought to involve carbon-metal bond cleavage for most cases which have been investigated. However, as long as the carbon-metal bond is chemically stable, the substitution of fluorine on the ring is feasible and thus three features for this type of reaction must be considered if reaction has occurred.

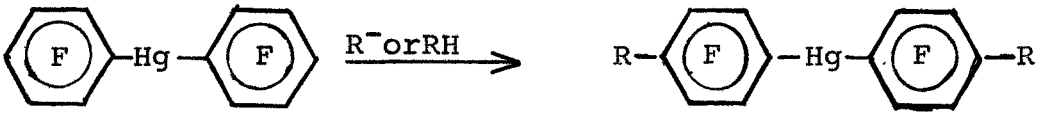
(1) the metal-C_6F_5 bond is cleaved completely.

(2) the metal-C_6F_5 is not cleaved at all and instead fluorines on the ring are replaced.

(3) mixed (1) and (2).

A few examples where nucleophic substitution of fluorine atom has taken place are given.

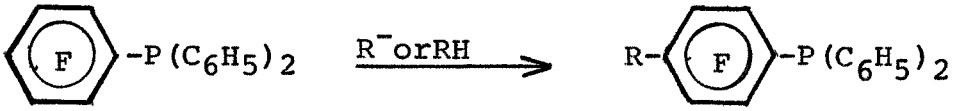
Bis(pentafluorophenyl) mercury is treated with KOH, CH_3ONa, and NH_2NH_2 (16) to form para-substituted products.



where $R^- = {}^-NHNH_2$, ^-OH and $^-OCH_3$

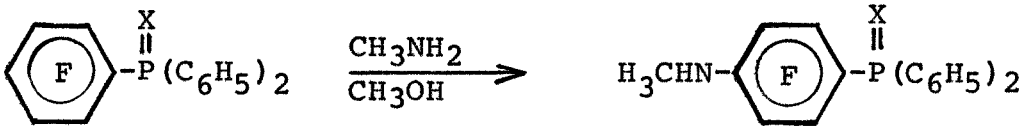
The same substituted compound is also found in the reaction of C_6F_5HgCl with CH_3ONa (16).

Pentafluorophenyldiphenylphosphine reacts with CH_3ONa and with CH_3NH_2 in benzene and ethanol to give the products in which substitution of the para-fluorine atom has occurred (17).



where $R^- = {}^-OCH_3$, $^-NHCH_3$.

Analogous reactions take place with the oxide and sulfide of pentafluorophenyldiphenylphosphine.



where X = O, S.

However, in benzene solution the formation of ortho-substitution products takes place. The substitution of both ortho and para-fluorine atoms in the reaction of $C_6F_5PCl_2$ with $NH(CH_3)_2$ has also been reported (18).

The reaction of pentafluorophenyldiphenylphosphine sulfide with CH_3ONa affords $P\text{-}CH_3OC_6F_4PS(C_6H_5)_2$ along with phosphorus-C_6F_5 bond cleavage product. In contrast, in the reaction of pentafluorophenyldiphenylphosphine oxide with CH_3ONa, only phosphorus-C_6F_5 bond cleavage products are obtained.

Pentafluorophenyltrimethylsilane reacts with $n\text{-}C_4H_9Li$ and with $(C_6H_5)_3SiLi$ to give para-substituted compounds in THF (19, 20);

where R = $n\text{-}C_4H_9$, $(C_6H_5)_3Si$.

The same para-substituted compound has also been reported in the reaction of pentafluorophenyltriphenylsilane with $(C_6H_5)_3SiLi$ (20). Gilman et al. (21) obtain (4-n-butyltetrafluorophenyl)-diphenylsilane by treating pentafluorophenyldiphenylsilane with $n\text{-}C_4H_9Li$. In the reaction of dichlorodimethylsilane with the mixture of 1,2,3,4-tetrafluorobenzene and $n\text{-}C_4H_9Li$, Haiduc et al. (22) also isolate products of substitution of the fluorine atom. More recently Sethi et al. (23) attain (4-t-butyltetrafluorophenyl)-t-butylmethylsilane and bis(t-butyltetrafluorophenyl)-methylsilane in the reaction of bis(pentafluorophenyl)-methylsilane and t-butyllithium.

Unlike general synthetic work, our work emphasizes the routine analysis of all the synthesis products by the G.C./M.S. technique. Therefore only a small amount of starting material is required and the control of reaction condition is less critical.

Pentafluorophenyllithium which is obtained from both pentafluorobenzene and bromopentafluorobenzene with n-butyllithium in ether/hexane was treated with

(1) C_6H_6, C_6F_5X (X = H, F, Cl, Br, I), o-$C_6F_4H_2$, m-$C_6F_4Cl_2$ and 1,3,5-$C_6F_3Cl_3$.

(2) $C_6F_5Si(CH_3)_3$ and $C_6H_5Si(CH_3)_3$.

(3) $(C_6F_5)_3P$, $(C_6H_5)_3P$; $(C_6F_5)_3P{=}O$, $(C_6H_5)_3P{=}O$.

(4) $(\pi\text{-}C_5H_5)_2Fe$.

The results of G.C./M.S. analysis of the reaction products are presented and discussed.

In addition, there is some evidence (24) which indicates that the halide in the magnesium halide may exchange with fluorine on the ring during the Grignard preparation of $(C_6F_5)_2Si(CH_3)_2$. More recently, other examples of this type of reversed halide exchange are also observed (25). Seeking further confirmation of this reaction, a series of reactions involving the treating of either pentafluorotrimethylsilane or bis(pentafluorophenyl)-dimethylsilane with either MgBrCl or LiCl directly from the reaction is also incorporated as part of our work.

2. Combined Gas Chromatography and Mass Spectrometry (G.C./M.S.) Techniques

I. History

The progress of science depends on many factors, but undoubtedly among the most important is the development of new experimental techniques. In chemical analysis of complicated organic mixtures, this is particularly well exemplified by the advent of the combined gas chromatograph/mass spectrometer. In 1910 Thomson first separated masses of an element and in 1919 Aston built his mass spectrograph. Mass spectroscopy as such has a long history, but it was not until the early 1940's that analytical mass spectrometers for the chemists appeared.

Initially these instruments were used for quantitative work in the petroleum industry until James and Martin in 1952 (26) introduced gas-liquid chromatography, a more powerful tool for separation and quantification. Thus freed from routine analytical work, mass spectroscopists turned their attention to develop the qualitative, molecular structure determination aspects of mass spectroscopy. The consequence of interdisciplinary stimulation along with the intrinsic compatibility existing between both techniques was immediately recognized. In 1957, five years after the invention of gas chromatography, Holmes and Morrell (27) started their first on-line G.C./M.S. attempt. In 1957, Gohlke (28) had achieved the first practical on-line G.C./M.S. (Time of Flight type mass spectrometer).

Unfortunately the very fast scan rate of first G.C./M.S. didn't show the particular advantages of the technique, since although 10,000 scans/second could be observed in an oscilloscope, records on paper could only be obtained over a period of a minute or more. Thus the attention was turned to the then well-developed magnetic sector type of mass spectrometer in the early 1960's, initially using accelerating scans, but by the late 1960's fast scanning magnets were in use. It was in the late 1960's the computer was first used for high resolution mass spectrometry. This idea was combined with the G.C./M.S. technique as technical problems were overcome and the first commercially available G.C./M.S. with on-line computer design came out shortly thereafter. Meanwhile another design, based on the quadrupole mass analyzer, capable of fast linear scans was developed and was readily interfaced to computers for medium-low resolution G.C./M.S. The popularity of G.C./M.S. instruments has since then flooded numerous analytical fields, especially for those which are dealing with complicated mixtures such as pharmaceuticals, toxicology, forensic, drug abuse, trace impurities, air and water pollution studies, etc.

II. Basic Principles

The individual components of the complicated mixtures, after the separation by the powerful gas chromatography technique go through the interface, in which the pressure is reduced by removal of carrier gas, directly into the ionization chamber of mass spectrometer. Here molecules are

ionized or cleaved into ions and then accelerated into the mass analyzer and detector. The signals are amplified and recorded on the ultraviolet sensitive paper using an oscillographic recorder.

It seems to be simple, but in fact a successful run largely depends on the complete understanding of the whole system including gas chromatograph, interface, mass spectrometer and vacuum system.

Several reviews (29 - 32) on this have appeared, and of these, McFadden's book (32) gives the most detailed information so far. Based on several years of operation experience of AEIMS-30 in the Department, Miller (33) also gives a brief, useful review, particularly emphasizing the application of organometallic compounds. As for the explanation and thus identification of mass spectrum, several books (34-36) will be the first choice.

III. Uses

Gas chromatography alone uses the retention time as a basis for qualitative analysis. The difficulty of the reproducibility of data is a handicap to this technique. In G.C./M.S. technique, the compound is directly identified from the mass spectrum and the uncertainty as to the identity of a peak is removed. However, the comparison of the retention time is helpful and offers one more support.

Relying on the unique features of speed and specificity G.C./M.S. can be used to solve day by day laboratory problems within a much shorter time than previously possible. Above

all, in a new synthetic mixture, the whole mixture of components is monitored and identified. It is fair to say this is a great aid in optimizing the synthetic conditions used and thus in improving the yield of the compound desired. Clues are also offered as to the most effective means of further purification. At times, some unexpected compounds can also be found and thus it is possible to redesign the experimental procedures to get new compounds.

IV. Feasibility of G.C./M.S. Techniques for This Work

As for G.C./M.S. analysis the volatility and thermal stability of compounds analyzed is of most importance. In addition to this, metal-catalyzed effects which may take place inside the instrument shouldn't be neglected.

Fluorocarbons are often more volatile than their hydrocarbon analogues, and this property does explain the extensive use of gas chromatography on the analysis of fluoro compounds since early developments (7). The choice of organometallic compounds is more critical, and careful attention to this choice has been made in this work.

EXPERIMENTAL AND RESULTS

I. Glass Apparatus for the Reactions of Air-sensitive Reagents

All reactions involving organo-magnesium and organo-lithium reagents are carried out in 50 ml. (or 100 ml.) three-necked flasks fitted with a reflux condenser, a pressure-equilibrated dropping funnel, a septum-cap and a Teflon-sealed magnetic stirrer bar inside under an atmosphere of dry, oxygen-free nitrogen. All glass-ware is baked in an oven at ca. 110°C prior to use and assembled, while hot, with a stream of nitrogen flowing through it.

II. Gas Chromatography

The preliminary analyses of the reaction mixtures are done on a Varian Aerograph 90-P3 gas chromatograph equipped with a thermal conductivity detector at various flow rates and column temperatures. A 5 ft. x 1/4 in. (I.D.) copper column packed with 3% SE-30 on Chromosorb W is used and helium is the carrier gas. The results are recorded on a Coleman Hitachi 165 potentiometric recorder with 1 mv./sec. full-scale deflection.

The purpose of this work is to test the feasibility of using SE-30 columns for each type of mixture and to search for the optimum operational parameters which are, more or less, helpful as references for the set-up of the conditions of later gas chromatographic/mass spectrometric runs. Occasionally, it is also used for checking the purities of

reagents.

III. Combined Gas Chromatography and Mass Spectrometry

Most of this work is carried out on an AEI MS-30 double beam, double focussing, mass spectrometer interfaced with a PYE 104 gas chromatograph through both a silicone membrane separator and a glass Biemann frit separator. The total ion monitor is used to obtain the gas chromatogram and indicate the proper time for mass scanning. The mass spectra are recorded using a Honeywell Y 3108 U.V. visicorder with response frequency of 5 KHz at either 3 or 10 sec./mass decade. Other operational parameters include accelerating voltage, 4 KV.; resolution, 1000; filament current, 100 μamp.; electron voltage, 70 e.v.; source temperature, 200°C; separator temperature, 250°C; connecting line temperature, 250°C; column temperature, programmed linearly from 50°C to 300°C at either 10°C or 15°C/min., and a He flow rate of 40-50 ml./min.

PFK (perfluorokerosene) is used as a mass marker in one beam, at the same time as the G.C. effluent is recorded in the other. The column is 5 ft. x 1/4 in. (I.D.) glass column packed with 3% SE-30 on Chromosorb W, the carrier gas is helium and Biemann separator is used.

IV. Sources and Pretreatments of Reagents and Solvents

Chemicals/Formula	Physical states under normal conditions	Sources	Pretreatments prior to use
anhydrous ethyl ether, $C_2H_5OC_2H_5$	colorless liquid	Malinckrodt	dried over sodium wire
benzene, C_6H_6	colorless liquid	B.D.H.	G.C. analysis and dried over sodium
bromobenzene, C_6H_5Br	colorless liquid	B.D.H.	G.C. analysis and dried over phosphorus pentoxide
bromopentafluorobenzene, C_6F_5Br	colorless liquid	Pierce	G.C. analysis and dried over phosphorus pentoxide
n-butyllithium (in hexane), $n\text{-}C_4H_9Li$	yellow solution	ALFA	used directly without further purification
chlorobenzene, C_6H_5Cl	colorless liquid	B.D.H.	G.C. analysis and dried over phosphorus pentoxide
chloropentafluorobenzene, C_6F_5Cl	colorless liquid	I.C.I.	G.C. analysis and dried over phosphorus pentoxide
o-dichlorobenzene, $C_6H_4Cl_2$	colorless liquid	B.D.H.	G.C. analysis and dried over phosphorus pentoxide
m-dichlorotetrafluoro-benzene, $C_6F_4Cl_2$	colorless liquid	I.C.I.	G.C. analysis and dried over phosphorus pentoxide

dicyclopentadienyl iron, $(\pi\text{-}C_5H_5)_2Fe$	Brown solid	Eastman	G.C. analysis and used directly without further purification
dimethyldichlorosilane, $(CH_3)_2SiCl_2$	colorless liquid	ALFA	redistillation and G.C. analysis
1,4-dioxane, $C_4H_8O_2$	colorless liquid	B.D.H.	G.C. analysis and dried over sodium
hexafluorobenzene, C_6F_6	colorless liquid	Whittaker	G.C. analysis and dried over phosphorus pentoxide
iodopentafluorobenzene, C_6F_5I	colorless liquid	Pierce	G.C. analysis and dried over phosphorus pentoxide
magnesium turnings, Mg	silver-gray metal	Fisher	washed with dry ether and dried in the oven
pentafluorobenzene, C_6F_5H	colorless liquid	Fluorochem.	G.C. analysis and dried over phosphorus pentoxide
pentafluorophenyltrimethylsilane, $C_6F_5Si(CH_3)_3$	colorless liquid	prepared as in step VII	redistillation and G.C. analysis
phenyltrimethylsilane, $C_6H_5Si(CH_3)_3$	colorless liquid	prepared as in step V	redistillation and G.C. analysis
1,2,3,4-tetrafluorobenzene, $C_6F_4H_2$	colorless liquid	Fluorochem.	G.C. analysis and dried over phosphorus pentoxide
toluene, $C_6H_5CH_3$	colorless liquid	B.D.H.	G.C. analysis and dried over sodium

1,3,5-trifluorotrichloro-benzene, $C_6F_3Cl_3$	white crystal	I.C.I.	G.C. analysis and used directly without further purification
trimethylchlorosilane, $(CH_3)_3SiCl$	colorless liquid	ALFA	redistillation and G.C. analysis
triphenylphosphine, $(C_6H_5)_3P$	white crystal	Eastman	G.C. analysis and used directly without further purification
triphenylphosphine Oxide, $(C_6H_5)_3P=O$	white crystal	Eastman	G.C. analysis and used directly without further purification
tris(pentafluorophenyl)-phosphine, $(C_6F_5)_3P$	white crystal	donated from Hanna	G.C. analysis and used directly without further purification
tris(pentafluorophenyl)-phosphine Oxide, $(C_6F_5)_3P=O$	white crystal	donated from Hanna	G.C. analysis and used directly without further purification

V. Preparation of Phenyltrimethylsilane

Trimethylchlorosilane (0.54 gm., 5 mmoles) is slowly added using a hypodermic syringe via a septum-cap into a phenyllithium solution, which is prepared from bromobenzene (0.79 gm., 5 mmoles) and n-butyllithium (0.27 gm., 5 mmoles) in ether/hexane (20 ml.), with vigorous stirring at -78°C (mixed dry-ice and alcohol bath). After the completion of addition, the reaction mixture is allowed to warm to room temperature and stirred for 2 hours. Cold water and dilute sulfuric acid are added, the organic layer separated is dried ($MgSO_4$) and filtered. Vacuum distillation gives phenyltrimethylsilane (0.42 gm.), a colorless liquid, which is characterized by mass spectrum (m/e = 150, 135, 119, 108, 106, 73, etc.).

VI. Preparation of Pentafluorophenylmagnesium Bromide Solution

Bromopentafluorobenzene (2.47 gm., 10 mmoles) is dropwise added into magnesium turnings (0.24 gm., 10 mmoles) in dry ether (15 ml.) with stirring over ca. 30 minutes at room temperature, followed by one hour's refluxing at this temperature. The pentafluorophenylmagnesium bromide, hereafter named solution A , is directly used for the following reactions without further treatment.

VII. Preparation of Pentafluorophenyllithium Solution

VII - 1. from Bromopentafluorobenzene

n-butyllithium (0.54 gm., 10 mmoles) in hexane (ca. 5 ml.) is dropwise added into bromopentafluorobenzene

(2.47 gm., 10 mmoles) in dry ether (15 ml.), and stirred for one hour at - 78° C . The pentafluorophenyllithium, hereafter named solution B , is directly used for the following reactions without further treatment.

VII - 2. from Pentafluorobenzene

n-Butyllithium (0.54 gm., 10 mmoles) in hexane (ca. 5 ml.) is dropwise added into pentafluorobenzene (1.68 gm., 10 mmoles) in dry ether (15 ml.) with stirring at -78°C, and stirred for 2 hours at this temperature. The pentafluorophenyllithium, hereafter named solution C , is directly used for the following reactions without further treatment.

VIII. Preparation of Pentafluorophenyltrimethylsilane

Trimethylchlorosilane (10.9 gm., 50 mmoles) is slowly added using a hypodermic syringe through a septum-cap into an approximately equivalent amount of solution C with vigorous stirring at -78°C. After the completion of addition, the reaction mixture is allowed to warm to room temperature and stirred for 2 hours. Cold water and dilute sulfuric acid are added, the organic layer separated is dried ($MgSO_4$), and filtered. Vacuum distillation gives pentafluorophenyltrimethylsilane (4.0 gm.), a colorless liquid; which is characterized by mass spectrum (m/e = 240, 225, 159, 129, 125, 81, 75, 73, etc.).

IX. Reactions of Pentafluorophenyltrimethylsilane under Grignard Conditions

IX - 1. in Ether

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution A with stirring at 0°C (ice-water bath), and stirred for 6 hours at room temperature. Cold water and dilute sulfuric acid are added, the organic layer separated is dried ($MgSO_4$), filtered and concentrated by vacuum distillation to ca. 1 ml. A dark-brown mixture is obtained. The results of G.C./M.S. analysis are given in Table-1.

IX - 2. in Benzene

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution A with stirring at 0°C. The reaction mixture is warmed to room temperature and most of the ether is removed by distillation and benzene (5 ml.) is added. After being stirred for 6 hours at ca. 45°C, it is cooled to room temperature and then cold water and dilute sulfuric acid are added. The organic layer is separated, dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. A dark-brown mixture is obtained. The results of G.C./M.S. analysis are given in Table-1.

IX - 3. in 1,4-Dioxane

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution A with stirring at 0°C. The reaction mixture is warmed to room temperature and most of the ether is removed and

1,4-dioxane (15 ml.) is added. The white solid is believed to be magnesium halide/1,4-dioxane complex. After being stirred for 6 hours at ca. 60°C, it is cooled to room temperature and then cold water and dilute sulfuric acid is added. The organic layer is separated, dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. A dark-brown mixture is obtained. The results of G.C./M.S. analysis are given in the Table-1.

IX - 4. in Chlorobenzene

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution A with stirring at 0°C. The reaction mixture is warmed to room temperature and most of the ether is removed and chlorobenzene (5 ml.) is added. After being stirred for 6 hours at ca. 80°C, it is cooled to room temperature and then cold water and dilute sulfuric acid are added. The organic layer was separated, dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. A dark-brown mixture is obtained. The results of G.C./M.S. analysis are given in the Table-1.

IX - 5. in o-Dichlorobenzene

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution A with stirring at 0°C. The reaction mixture is warmed to room temperature and most of the ether is removed and o-dichlorobenzene (5 ml.) is added. After being stirred for 6 hours at ca. 100°C, it is cooled to room temperature and then cold water and dilute sulfuric acid are added. The organic layer

Table-1. Reactions of $C_6F_5Si(CH_3)_3$ with Grignard Reagents

Reaction No.	Reagents	Solvents	Time/Temp.	Products
IX-1	$C_6F_5Si(CH_3)_3$	ether	6 hrs./r.t.	$A_1^{\ddagger}$; $(CH_3)_3SiO(Si(CH_3)_2O)_2Si(CH_3)_3^{\Delta}$
IX-2	$C_6F_5Si(CH_3)_3$	benzene	6 hrs./45°C	A_1; $B_1^{\S}$; C_6H_6
IX-3	$C_6F_5Si(CH_3)_3$	1,4-dioxane	6 hrs./60°C	A_1; B_1; $C_4H_8O_2$
IX-4	$C_6F_5Si(CH_3)_3$	chlorobenzene	6 hrs./80°C	A_1; B_1; C_6H_5Cl
IX-5	$C_6F_5Si(CH_3)_3$	o-dichloro-benzene	6 hrs./100°C	A_1; B_1; $C_6H_4Cl_2$

$^{\ddagger}A_1$ = $(C_2H_5)_2O$; C_6F_5H; $(CH_3)_3SiOSi(CH_3)_3$; C_6F_5Br; C_6F_4BrH; $C_6F_5Si(CH_3)_3$ (major); $(C_6F_5)_2$; $C_6F_4Br_2$; $C_{12}F_9H$.

$^{\S}B_1$ = $(CH_3)_3SiO(Si(CH_3)_2O)_nSi(CH_3)_3$, n=2,3.

$^{\Delta}$ Not enough information for the confirmation of the compounds.

is separated, dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. A dark-brown mixture is obtained. The results of G.C./M.S. analysis are given in the Table-1.

X. Reactions of Bis(pentafluorophenyl)dimethylsilane under Grignard Conditions

The parallel experiments to steps IX-1, IX-2, IX-3 and IX-4 are employed. In each case, dimethyldichlorosilane (6.45 gm., 5 mmoles) is used instead of trimethylchlorosilane. Work-up gives a dark-brown mixture. The results of G.C./M.S. analysis are shown in Table-2.

XI. Reactions of Pentafluorophenyltrimethylsilane with Lithium Reagents

XI - 1. in Ether/Hexane

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution C with stirring at -78°C. The reaction mixture is then warmed to room temperature and stirred for 6 hours. Cold water and dilute sulfuric acid are added, the organic layer separated was dried ($MgSO_4$), filtered, and concentrated to ca. 1 ml. A yellow mixture is obtained. The results of G.C./M.S. are given in the Table-3.

XI - 2. in Ether/Hexane and in the Presence of n-Butylbromide

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution B with stirring at -78°C. The reaction mixture is then warmed to room temperature and stirred for 6 hours. Cold water and dilute sulfuric acid are added, the organic layer separated

Table-2. Reactions of $(C_6F_5)_2Si(CH_3)_2$ with Grignard Reagents

Reaction No.	Reagents	Solvents	Time/Temp.	Products
X-1	$(C_6F_5)_2Si(CH_3)_2$	ether	6 hrs./r.t.	A_2^*; $B_2^\S$
X-2	$(C_6F_5)_2Si(CH_3)_2$	benzene	6 hrs./45°C	A_2; B_2; C_6H_6
X-3	$(C_6F_5)_2Si(CH_3)_2$	1,4-dioxane	6 hrs./60°C	A_2; B_2; $C_4H_8O_2$
X-4	$(C_6F_5)_2Si(CH_3)_2$	chlorobenzene	6 hrs./80°C	A_2; B_2; C_6H_5Cl
X-5	$(C_6F_5)_2Si(CH_3)_2$	o-dichloro-benzene	6 hrs./100°C	A_2; B_2; $C_6H_4Cl_2$

*A_2 = $(C_2H_5)_2O$; C_6F_5H; C_6F_4BrH; C_6F_5Br; $C_6F_5Si(CH_3)_3$; $(C_6F_5)_2$; $C_6F_4Br_2$; $(C_6F_5)_2Si(CH_3)_2$ (major).

§B_2 = $((CH_3)_2SiO)_n$, n = 3~12; $C_6F_5(Si(CH_3)_2O)_nSi(CH_3)_2C_6F_5$, n = 1~6.

In addition, eight regular G.C.-separated peaks whose molecular ions appear at 392, 466, 540, etc., respectively are unidentified.

is dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. A yellow mixture is obtained. The results of G.C./M.S. analysis are given in the Table-3.

XI - 3. in Toluene

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution C with stirring at -78°C. The reaction mixture is warmed to room temperature and most of the solvent is removed by distillation and toluene (5 ml.) is added. After being stirred for 6 hours at ca. 80°C, it is cooled to room temperature and then cold water and dilute sulfuric acid are added. The organic layer is separated, dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. A yellow mixture is obtained. The results of G.C./M.S. analysis are given in the Table-3.

XI - 4. in Toluene and in the presence of n-Butylbromide

Trimethylchlorosilane (1.09 gm., 10 mmoles) is slowly added to an approximately equivalent amount of solution B with stirring at -78°C. The reaction mixture is warmed to room temperature and most of the solvent is removed and toluene (5 ml.) is added. After being stirred for 6 hours at ca. 80°C, it is cooled to room temperature and then cold water and dilute sulfuric acid are added. The organic layer is separated, dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. A yellow mixture is obtained. The results of G.C./M.S. analysis are given in the Table-3.

Table-3. Reactions of $C_6F_5Si(CH_3)_3$ with Lithium Reagents

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XI-1	$C_6F_5Si(CH_3)_3$	ether/n-hexane	6 hrs./r.t.	$A_3^{\ddagger}$
XI-2*	$C_6F_5Si(CH_3)_3$	ether/n-hexane	6 hrs./r.t.	A_3; $B_3^{\S}$
XI-3	$C_6F_5Si(CH_3)_3$	toluene/ n-hexane	6 hrs./80°C	A_3; $C_6H_5CH_3$; $C_6F_5Si(CH_3)_2OSi(CH_3)_3^{\triangle}$✓; $n\text{-}C_4H_9C_6F_4Si(CH_3)_3$✓; $(C_6F_5)_2Si(CH_3)_2$✓
XI-4*	$C_6F_5Si(CH_3)_3$	toluene/ n-hexane	6 hrs./80°C	A_3; B_3; $C_6F_4Br_2$; $C_6H_5CH_3$; $(C_6F_5)_2Si(CH_3)_2$✓.

$^{\ddagger}A_3$ = $(C_2H_5)_2O$; $n\text{-}C_6H_{14}$; C_6F_5H; $(CH_3)_3SiOSi(CH_3)_3$; $n\text{-}C_8H_{18}$; $(n\text{-}C_4H_9O)Si(CH_3)_3$; $C_6F_5Si(CH_3)_3$ (major); $(CH_3)_3SiO(Si(CH_3)_2O)_2Si(CH_3)_3^{\triangle}$.

$^{\S}B_3$ = $n\text{-}C_4H_9Br$; C_6F_5Br.

*Reactions proceed under the presence of $n\text{-}C_4H_9Br$.

$^{\triangle}$ Uncertain because of not enough information.

✓ Detected under more concentrated condition.

XII. Reactions of Bis(pentafluorophenyl)dimethylsilane with Lithium Reagents

The parallel experiments to steps XI-1, XI-2, XI-3 and XI-4 are employed. In each case, dimethyldichlorosilane (6.45 gm., 5 mmoles) is used instead of trimethylchlorosilane. Work-up gives a yellow mixture. The results of G.C./M.S. analyses are shown in Table-4.

XIII. Decomposition Reactions of Pentafluorophenyllithium

XIII - 1. with Trimethylchlorosilane in the presence of Excess of Pentafluorobenzene

To solution C in which excess of pentafluorobenzene is present, trimethylchlorosilane (0.87 gm., 8 mmoles) is added with stirring and then the reaction mixture is warmed to room temperature. After being stirred for 6 hours, cold water and dilute sulfuric acid are added. The organic layer is separated and filtered to give a white solid which is washed with ether and analyzed by mass spectrometer through direct probe inlet. The ether solution is dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. to give a pale-yellow mixture. The results of M.S. and G.C./M.S. analyses are shown in the Table-5.

XIII - 2. with Trimethylchlorosilane in the presence of Excess of Bromopentafluorobenzene

To solution B in which excess of bromopentafluorobenzene is present, trimethylchlorosilane (0.87 gm., 8 mmoles) is added with stirring and then the reaction mixture is warmed to room temperature. After being stirred for 6 hours, cold water and dilute sulfuric acid are added. The organic layer

Table-4. Reactions of $(C_6F_5)_2Si(CH_3)_2$ with Lithium Reagents

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XII-1	$(C_6F_5)_2Si(CH_3)_2$	ether/n-hexane	6 hrs./r.t.	A_4^*
XII-2*	$(C_6F_5)_2Si(CH_3)_2$	ether/n-hexane	6 hrs./r.t.	A_4; $n\text{-}C_4H_9Br$; $(n\text{-}C_4H_9C_6F_4)(C_6F_5)Si(CH_3)_2$; $(n\text{-}C_4H_9C_6F_4)_2Si(CH_3)_2$.
XII-3	$(C_6F_5)_2Si(CH_3)_2$	toluene/ n-hexane	6 hrs./80°C	A_4; $C_6H_5CH_3$.
XII-4*	$(C_6F_5)_2Si(CH_3)_2$	toluene/ n-hexane	6 hrs./80°C	A_4; $n\text{-}C_4H_9Br$; $C_6H_5CH_3$.

*A_4 = $(C_2H_5)_2O$; $n\text{-}C_6H_{14}$; C_6F_5H; $((CH_3)_2SiO)_n$, n=3~7; $C_6F_5(Si(CH_3)_2O)_nSi(CH_3)_2OH$; n = 0~3; n → C_8H_{18}; $(CH_3)_2(n\text{-}C_4H_9)Si(C_6F_5)$; $(C_6F_5)_2Si(CH_3)_2$ (major).

*Reactions proceed under the presence of $n\text{-}C_4H_9Br$.

is separated and filtered to give a white solid which is washed with ether and analyzed by mass spectrometer through direct probe inlet. The ether solution is dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. to give a pale-yellow mixture. The results of M.S. and G.C./M.S. analyses are shown in the Table-5.

XIII - 3. with Benzene

Benzene (0.78 gm., 10 mmoles) is added to an approximately equivalent amount of solution C at -78°C. The reaction mixture is gradually warmed to room temperature and stirred for 6 hours. Cold water and dilute sulfuric acid are added, the organic layer separated and filtered to give a white solid which is washed with ether and analyzed by mass spectrometer through direct probe inlet. The ether solution is dried ($MgSO_4$), filtered and concentrated to ca. 1 ml. to give an orange-yellow mixture. The results of M.S. and G.C./M.S. analyses are shown in the Table-6.

XIII - 5. - XIII - 34.

The reactions XIII-5 to XIII-34 which are parallel to either XIII-3 or XIII-4 are presented in the Table. All the procedures employed are substantially the same as XIII-3 and XIII-4.

Table-5. Decomposition Reactions of C_6F_5Li with $(CH_3)_3SiCl$ in excess of C_6F_5X, (x=H, Br)

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XIII-2*	$(CH_3)_3SiCl$; excess C_6F_5Br	ether/ n-hexane	6 hrs./r.t.	A_5^*; C_6F_4HCl; $C_{6n}F_{4n+1}H$, n = 1~3; $(C_6F_5)_2$; $C_6F_4Br_2$; $C_{6n}F_{4n+1}Br$, n = 1~3.
XIII-1	$(CH_3)_3SiCl$; excess C_6F_5H	ether/ n-hexane	6 hrs./r.t.	A_5; $C_{6n}F_{4n}HCl$, n = 1~3; $C_{6n}F_{4n+1}H$, n = 1~5.

*A_5 = $(C_2H_5)_2O$; n-C_6H_{14}; $(CH_3)_3SiOSi(CH_3)_3$; $C_6F_4H_2$; n-C_8H_{18}; $C_6F_5Si(CH_3)_3$.

*Reaction proceeds under the presence of n-C_4H_9Br.

Reaction No.	with n-BuBr Reaction No.	Reagents (mmoles)	C_6F_5Li (mmoles)	Color of Product		Results to be found in Table no.	
				ether fraction	solid		
XIII-5	XIII-6	$O\text{-}C_6F_4H_2$ (10)	10	orange-yellow	white	8	8
XIII-7	XIII-8	C_6F_5H (10)	10	pale-yellow	white	6	7
XIII-9	XIII-10	C_6F_6 (10)	10	pale-yellow	white	6	7
XIII-11	XIII-12	C_6F_5Cl (10)	10	orange-yellow	white	6	7
XIII-13	XIII-14	$m\text{-}C_6F_4Cl_2$ (10)	10	orange-yellow	white	8	8
XIII-15	XIII-16	$1,3,5\text{-}C_6F_5Cl_3$ (10)	10	orange-yellow	white	8	8
XIII-17	XIII-18	C_6F_5Br (10)	10	pale-yellow	white	6	7
XIII-19	XIII-20	C_6F_5I (10)	10	pale-yellow	white	6	7
XIII-21	XIII-22	$C_6F_5Si(CH_3)_3$ (5)	5	pale-yellow	white	9	9
XIII-23	XIII-24	$C_6H_5Si(CH_3)_3$ (1)	1	pale-yellow	white	9	9
XIII-25	XIII-26	$(C_6F_5)_3P$ (3.3)	10	orange-yellow	white	10	10
XIII-27	XIII-28	$(C_6H_5)_3P$ (3.3)	10	dark-brown	white	10	10
XIII-29	XIII-30	$(C_6F_5)_3P{=}O$ (3.3)	10	pale-yellow	white	10	10
XIII-31	XIII-32	$(C_6H_5)_3P{=}O$ (3.3)	10	pale-yellow	white	10	10
XIII-33	XIII-34	$(\pi\text{-}C_5H_5)_2Fe$ (5.0)	10	dark-brown	white	11	11

Table-6. Reactions of C_6F_5Li with C_6F_5X, (X = H, F, Cl, Br, I) and C_6H_6, respectively

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XIII-3	C_6H_6	ether/n-hexane	6 hrs./r.t.	A_6^*; C_6H_6; $C_{6n}F_{4n}C_6H_6$, n = 1,2; $C_{6n}F_{4n+1}H$, n = 1 ~ 4; $C_{6n}F_{4n}H_2$, n = 2 ~ 4.
XIII-7	C_6F_5H	ether/n-hexane	6 hrs./r.t.	A_6; $C_{6n}F_{4n+1}H$, n = 1 ~ 5; $C_{6n}F_{4n}H_2$, n = 1 ~ 3.
XIII-9	C_6F_6	ether/n-hexane	6 hrs./r.t.	A_6; $C_{6n}F_{4n+1}H$, n = 1 ~ 4; $C_{6n}F_{4n+2}$, n = 1 ~ 4; $C_{6n}H_{4n}H_2$, n = 1 ~ 4; $(n\text{-}C_4H_9)C_6F_5$; $(n\text{-}C_4H_9)_2C_6F_4$.
XIII-11	C_6F_5Cl	ether/n-hexane	6 hrs./r.t.	A_6; $C_{6n}F_{4n+1}H$, n = 1 ~ 5; $C_{6n}F_{4n+1}Cl$, n = 1 ~ 5; $C_{6n}F_{4n}H_2$, n = 1 ~ 4.
XIII-17	C_6F_5Br	ether/n-hexane	6 hrs./r.t.	A_6; $n\text{-}C_4H_9Br$; $C_{6n}F_{4n+1}H$, n = 1 ~ 4; $C_{6n}F_{4n+1}Br$, n = 2 ~ 4; $C_{6n}F_{4n}Br_2$, n = 1 ~ 3.
XIII-19	C_6F_5I	ether/n-hexane	6 hrs./r.t.	A_6; $n\text{-}C_4H_9I$; $C_{6n}F_{4n+1}H$,

Table-6 (Continued)

$n = 1, 2$; $C_{6n}F_{4n+1}I$, $n = 2, 3$; $C_{6n}F_{4n}I_2$, $n = 1, 2$.

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*$A_6 = (C_2H_5)_2O$; $n\text{-}C_6H_{14}$; $n\text{-}C_8H_{18}$.

Table-7. Reactions of C_6F_5Li with C_6F_5X, (X = H, F, Cl, Br, I) and C_6H_6 in the Presence of n-C_4H_9Br, respectively.

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XIII-4	C_6H_6	ether/ n-hexane	6 hrs./r.t.	A_7^*; C_6H_6; $C_{6n}F_{4n}C_6H_6$, n = 1, 2. $C_{6n}F_{4n+1}H$, n = 1, 2.
XIII-8	C_6F_5H	ether/ n-hexane	6 hrs./r.t.	A_7; $C_{6n}F_{4n+1}H$, n = 1～5; $C_{6n}F_{4n}H_2$, n = 1～3; $C_{6n}F_{4n}HBr$, n = 2, 3; $C_{6n}F_{4n+1}Br$, n = 2, 3.
XIII-10	C_6F_6	ether/ n-hexane	6 hrs./r.t.	A_7; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n}H_2$, n = 1～4; $C_{6n}F_{4n+2}$, n = 1～5; $C_{6n}F_{4n+1}Br$, n = 2, 3; $C_6F_5(n\text{-}C_4H_9)$; $C_6F_4(n\text{-}C_4H_9)_2$.
XIII-12	C_6F_5Cl	ether/ n-hexane	6 hrs./r.t.	A_7; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n}H_2$, n = 1～3; $C_{6n}F_{4n+1}Br$, n = 2～5; $C_{6n}F_{4n}Br_2$, n = 2, 3; $C_{6n}F_{4n+1}Cl$, n = 1～3.
XIII-18	C_6F_5Br	ether/ n-hexane	6 hrs./r.t.	A_7; $C_{6n}F_{4n+1}H$, n = 1～5; $C_{6n}F_{4n+1}Br$, n = 1～4; $C_{6n}F_{4n}Br_2$, n = 1～3.

Table-7 (Continued)

XIII-20	C_6F_5I	ether/ n-hexane	6 hrs./r.t.	A_7; $C_{6n}F_{4n+1}H$, n = 1 ~ 3; $C_{6n}F_{4n+1}Br$, n = 1 ~ 3; $C_{6n}F_{4n+1}I$, n = 1 ~ 3; $C_{6n}F_{4n}I_2$, n = 1, 2; $C_{6n}F_{4n}IBr$, n = 1, 2. C_6F_4HI.

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*A_7 = $(C_2H_5)_2O$; n-C_6H_{14}; n-C_8H_{18}; n-C_4H_9Br.

Table-8. Reactions of C_6F_5Li with $C_6F_4X_2$, (X=H, Cl) and $C_6F_3Cl_3$, respectively.

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XIII-5	$C_6F_4H_2$	ether/ n-hexane	6 hrs./r.t.	A_8^*; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n}H_2$, n = 1～4; $C_{6n}F_{4n+2}$, n = 2～4.
XIII-13	$C_6F_4Cl_2$	ether/ n-hexane	6 hrs./r.t.	A_8; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n}H_2$, n = 2,3; $C_{6n}F_{4n+1}Cl$, n = 2～4; $C_{6n}F_{4n}Cl_2$, n = 1～3.
XIII-15	$C_6F_3Cl_3$	ether/ n-hexane	6 hrs./r.t.	A_8; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n}H_2$, n = 3, 4; $C_{6n}F_{4n+1}Cl$, n = 2～4; $C_{6n}F_{4n-1}Cl_3$, n = 1～4.
XIII-6*	$C_6F_4H_2$	ether/ n-hexane	6 hrs./r.t.	B_8^*; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n}H_2$, n = 1～4; $C_{6n}F_{4n+2}$, n = 2～4; $C_{6n}F_{4n+1}Br$, n = 2～4; $C_{6n}F_{4n}Br_2$, n = 2, 3.
XIII-14*	$C_6F_4Cl_2$	ether/ n-hexane	6 hrs./r.t.	B_8; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n+1}Cl$, n = 2～4; $C_{6n}F_{4n}Cl_2$, n = 1～3; $C_{6n}F_{4n+1}Br$, n = 2～4; $C_{18}F_{12}Br_2$.
XIII-16*	$C_6F_3Cl_3$	ether/ n-hexane	6 hrs./r.t.	B_8; $C_{6n}F_{4n+1}H$, n = 1～4; $C_{6n}F_{4n+1}Cl$, n = 2,3; $C_{6n}F_{4n-1}Cl_3$, n = 1～4;

Table-8 (Continued)

$C_{6n}F_{4n+1}Br$, n = 2 ~ 4; $C_{18}F_{12}Br_2$.

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†A_8 = $(C_2H_5)_2O$; n-C_6H_{14}; n-C_8H_{18}.

§B_8 = A_8; n-C_4H_9Br.

*Reactions proceed under the presence of n-C_4H_9Br.

Table-9. Reactions of C_6F_5Li with $(C_6X_5)Si(CH_3)_3$, (X = H, F), respectively.

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XIII-23	$C_6H_5Si(CH_3)_3$	ether/ n-hexane	6 hrs./r.t.	$A_9^{\natural}$; C_6H_5Br; $C_6H_5Si(CH_3)_3$; $C_{6n}F_{4n+1}H$, n = 1 ~ 4; $C_{6n}F_{4n}H_2$, n = 1 ~ 3.
XIII-21	$C_6F_5Si(CH_3)_3$	ether/ n-hexane	6 hrs./r.t.	A_9; $C_6F_5Si(CH_3)_3$; $C_{6n}F_{4n+1}H$, n = 1 ~ 4; $C_6F_4H_2$, $C_{6n}F_{4n+2}$, n = 2 ~ 4; n-$C_4H_9C_6F_4Si(CH_3)_3$.
XIII-24*	$C_6H_5Si(CH_3)_3$	ether/ n-hexane	6 hrs./r.t.	$B_9^{\natural}$; C_6H_5Br; $C_6H_5Si(CH_3)_3$; $C_{6n}F_{4n+1}H$, n = 1 ~ 5; $C_{6n}F_{4n}H_2$, n = 2 ~ 4; $C_{6n}F_{4n+2}$, n = 2 ~ 4; $C_{6n}F_{4n+1}Br$, n=2 ~ 4; $C_{12}F_8HBr$.
XIII-22*	$C_6F_5Si(CH_3)_3$	ether/ n-hexane	6 hrs./r.t.	B_9; $C_6F_5Si(CH_3)_3$; $C_{6n}F_{4n+1}H$, n = 1 ~ 4; $C_6F_4H_2$; $C_{6n}F_{4n+2}$, n = 2 ~ 4; $C_{6n}F_{4n+1}Br$, n = 2 ~ 4; $C_{6n}F_{4n}Br_2$, n = 1 ~ 3; $C_{12}F_8HBr$; n-$C_4H_9C_6F_4Si(CH_3)_3$.

$^{\natural}A_9$ = $(C_2H_5)_2O$; n-C_6H_{14}; n-C_8H_{18}. $^{\natural}B_9$ = A_9; n-C_4H_9Br.

*Reactions proceed under the presence of n-C_4H_9Br.

Table-10. Reactions of C_6F_5Li with $(C_6X_5)_3P$ and $(C_6X_5)_3P{=}O$, (X = H, F), respectively.

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XIII-27	$(C_6H_5)_3P$	ether/ n-hexane	6 hrs./r.t.	A_{10}^{*}; $C_{6n}F_{4n+1}H$, n = 1∼4; $C_{24}F_{16}H_2$; $(C_6H_5)_3P$.
XIII-25	$(C_6F_5)_3P$	ether/ n-hexane	6 hrs./r.t.	A_{10}; $C_{6n}F_{4n+1}H$, n = 1∼4; $C_{6n}F_{4n}H_2$, n = 2, 3; $(C_6F_5)_3P$; $(C_6F_5)_2(C_{12}F_9)P$; $(C_6F_5)(C_{12}F_9)_2P$; $(C_{12}F_9)_3P$.
XIII-28*	$(C_6H_5)_3P$	ether/ n-hexane	6 hrs./r.t.	$B_{10}^{\frac{1}{2}}$; $C_{6n}F_{4n+1}H$, n = 1∼4; $C_{6n}F_{4n}H_2$, n = 1∼4; $C_{6n}F_{4n+1}Br$, n = 2, 3; $C_{6n}F_{4n}HBr$, n = 1, 2; $(C_6H_5)_3P$; $(C_6F_5)_3P$; $(C_{12}F_9)(C_6F_5)_2P$.
XIII-26*	$(C_6F_5)_3P$	ether/ n-hexane	6 hrs./r.t.	B_{10}; $C_{6n}F_{4n+1}H$, n = 1∼4; $C_6F_4H_2$; $C_{6n}F_{4n+1}Br$, n = 1∼4; $C_{6n}F_{4n}Br_2$, n = 1∼3; $C_{6n}F_{4n+2}$, n = 2, 3; $C_{12}F_8HBr$; $(C_6F_5)_3P$; $(C_6F_5)_2(C_{12}F_9)P$.
XIII-31	$(C_6H_5)_3P{=}O$	ether/ n-hexane	6 hrs./r.t.	A_{10}; $C_{6n}F_{4n+1}H$, n = 1∼4; $(C_6H_5)_3P{=}O$.
XIII-29	$(C_6F_5)_3P{=}O$	ether/ n-hexane	6 hrs./r.t.	A_{10}; $C_{6n}F_{4n+1}H$, n = 1∼4; $C_{12}F_{10}$; $(C_6F_5)_3P$, $(C_6F_5)_2(C_{12}F_9)P$; $(C_6F_5)_3P{=}O$.

Table-10 (Continued)

XIII-32*	$(C_6H_5)_3P=O$	ether/ n-hexane	6 hrs./r.t.	B_{10}; $C_{6n}F_{4n+1}H$, n = 1∼4; $C_{6n}F_{4n+1}Br$, n = 2∼4; $(C_6H_5)_3P=O$.
XIII-30*	$(C_6F_5)_3P=O$	ether/ n-hexane	6 hrs./r.t.	B_{10}; $C_{6n}F_{4n+1}H$, n = 1∼4; $C_{6n}F_{4n+1}Br$, n = 1∼4; $C_{12}F_8HBr$; $(C_6F_5)_3P$; $(C_6F_5)_2(C_{12}F_9)P$; $(C_6F_5)_3P=O$.

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*A_{10} = $(C_2H_5)_2O$; n-C_6H_{14}; n-C_8H_{18}.

♮B_{10} = A_{10}; n-C_4H_9Br.

*Reactions proceed under the presence of n-C_4H_9Br.

Table-11. Reactions of C_6F_5Li with $(\pi\text{-}C_5H_5)_2Fe$.

Reaction No.	Reagents	Solvents	Time/Temp.	Products
XIII-33	$(\pi\text{-}C_5H_5)_2Fe$	ether/ n-hexane	6 hrs./r.t.	A_{11}^{*}; $C_{6n}F_{4n+1}H$, n = 1~5; $C_{6n}F_{4n}H_2$, n = 1~4; $(\pi\text{-}C_5H_5)_2Fe$; $(\pi\text{-}C_5H_4C_6F_4H)(\pi\text{-}C_5H_5)Fe$.
XIII-34*	$(\pi\text{-}C_5H_5)_2Fe$	ether/ n-hexane	6 hrs./r.t.	A_{11}; $n\text{-}C_4H_9Br$; $C_{6n}F_{4n+1}H$, n = 1~4; $C_{6n}F_{4n}H_2$, n = 3, 4; $C_{6n}F_{4n+1}Br$, n = 2~5; $C_{18}F_{12}Br_2$; $(\pi\text{-}C_5H_5)_2Fe$.

*A_{11} = $(C_2H_5)_2O$; $n\text{-}C_6H_{14}$; $n\text{-}C_8H_{18}$.

*Reaction proceeds under the presence of $n\text{-}C_4H_9Br$.

DISCUSSION

1. G.C./M.S. Method Used as Routine Tool for Monitoring Synthetic Mixtures

Three main questions can be formulated in any analytical situation: methods, materials and problems. Our work involves using the G.C./M.S. method to analyze synthetic mixtures and the results acquired are discussed. To achieve our final purposes, it is imperative that further consideration of the analytical procedures is required.

To obtain satisfactory performance of a G.C./M.S. combination, operation of the gas chromatograph, the interface and the mass spectrometer must all be optimized. The whole procedure of G.C./M.S. operation involves many factors and will briefly be probed.

I. Selection of Separator

Two of the most important factors concerning the performance of an interface are sensitivity and resolution. Sensitivity of the interface can be considered as that proportion of the actual sample which finds its way from the column effluent to the ion source of the mass spectrometer and the resolution is a measure of the amount of change of the chromatographic resolution of the column by the interface. The optimization of sensitivity must not be at the expense of change in the chromatographic resolution of the column. There are two choices in our AEI-MS-30; one is a silicone rubber membrane separator which involves the

dissolution of sample in the membrane and the diffusion into the mass spectrometer, and the other is a glass frit Biemann separator which operates according to the principle of effusion under the condition of molecular flow. Based on the considerations of the mass of sample and the maximum operating temperature used, which for the former separator is restricted to about 250°C because the bleeding and thermal stability of the silicone rubber may be serious at higher temperature, the glass frit Biemann separator is thus chosen and its simplified structure is shown in Fig. 1. The glass surface also provides a reasonable inertness to prevent decomposition of delicate components and its regeneration after use over a long period can simply be by heating to a higher temperature and then silanizing.

II. Gas Chromatography

The sharpness of a G.C. peak is an important factor in determining the utilization of the sample in G.C./M.S. Some of the factors that affect peak sharpness are: (i) % load of a stationary phase; (ii) carrier gas flow rate; (iii) temperature, and (iv) type and length of column. Generally speaking, for most G.C./M.S. work the stationary phase load should not exceed 4-5%. Larger sample charge from a higher percentage stationary phase may not improve the sharpness of low abundance chromatographic peaks and may be of minimal value if the chromatographic peaks are broadened.

Use of higher temperature often leads to sharper

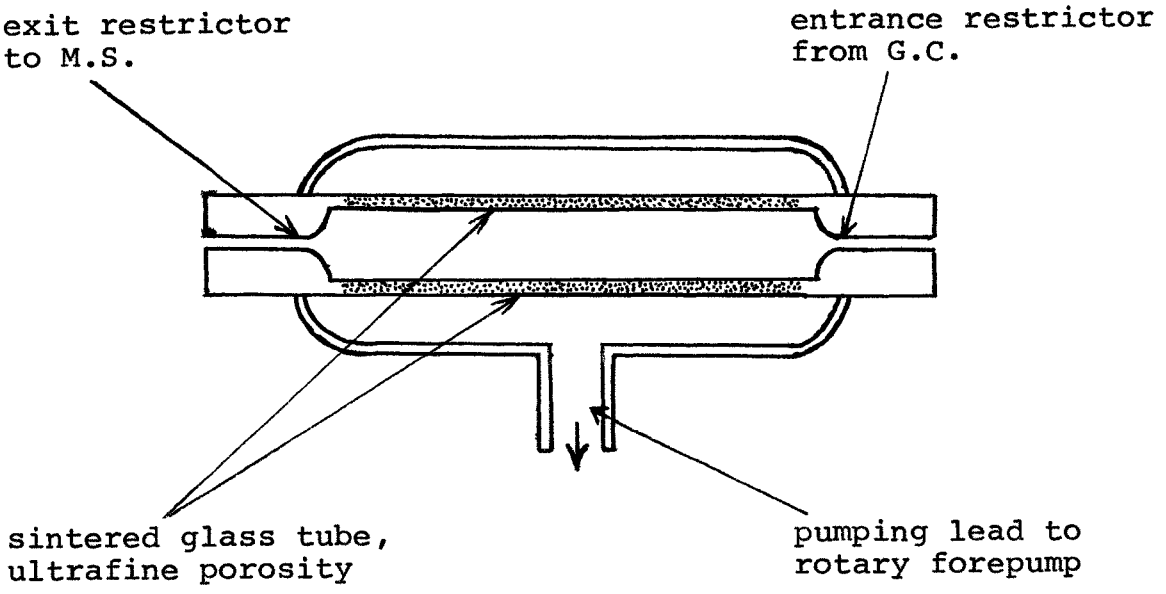


Fig. 1. Watson-Biemann Effusion Separator; it is mounted in a heated oven.

peaks. When the resolution is sufficient, a fast temperature programming is advantageous for analyzing a complex mixture with wide range of boiling points of components. If column bleeding and thermal decomposition are suspected, a fast flow rate might be considered to get sharp peaks. It is well known that even a factor of four or five increase in the flow rate may not cause significant waste of sample (32) which is subjected to enrichment by the interface, and this is because sharp peaks permit more sample per second to enter the mass spectrometer, thus relatively increasing sensitivity.

As mentioned earlier in the experimental section, a conventional G.C. run of a sample should be made to obtain the best column for maximum separation, optimum temperature and flow rate prior to submitting to a G.C./M.S. analysis. After several trial and error runs, a nonpolar stationary phase, namely SE-30 with the composition $(CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$ was selected and it was packed with 3% of stationary phase on Chromosorb W support in a glass column to minimize the catalytic activity which might occur on the metal surface; for example, in this work C_6F_5Br can be catalyzed by activated copper at high temperature to form C_6F_5-C_6F_5. However C_6F_5Br can be eluted from the column before any appreciable reaction takes place. The reason for one column serving well for this work may simply be attributed to the similarities of types of samples analyzed.

III. Temperature Control in The G.C./M.S. Interface

According to the general principle, if the column is temperature programmed the interface temperature should be held at maximum column temperature. Practically the interface temperature can be set lower than the maximum column temperature and this mainly takes advantage of the property that any organic material has a lower vapor pressure in equilibrium with the chromatographic stationary phase than in equilibrium with a clean metal or glass surface. How much lower it can be set is not well established, and it depends on the nature of the stationary phase, the sample analyzed and the history of the interface. If a column works well, as a rule, any suspicious observation on G.C. peak tailing (Fig. 2), which may be caused by the adsorption of sample on the surface of the interface including the connecting lines, may indicate that cold spots have appeared. A higher temperature will then be required.

Temperature of the ionization chamber which is under high vacuum was kept at 200°C and higher temperatures were seldom necessary even when the column was temperature programmed up to 250°-300°C.

IV. Limit of Pressure in The Ion Source of Mass Spectrometer

The maximum pressure which will avoid ion-molecule reactions and source sensitivity deteriorization can be used. Usually 2-5 $\mu l.$ of sample is satisfactory to attain the required result. If the mass spectrum of a low abundance component must be improved, it can be obtained by injecting

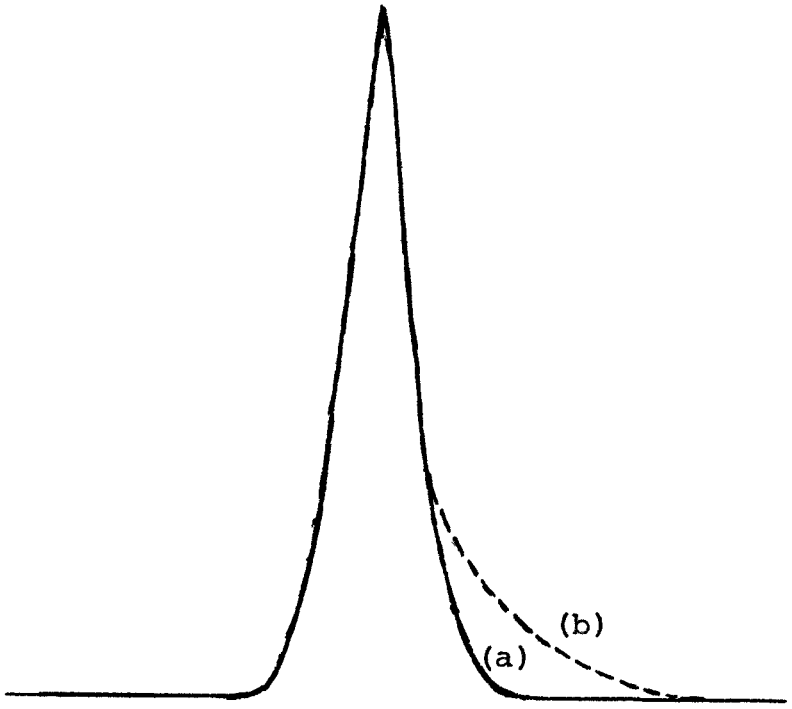


Fig. 2

A G.C. Peak Due to Adsorption

(a) solid line; normal peak. (b) dotted line; tailing peak.

more sample and venting high abundance components to avoid overloading the source. It should not be forgotten that injection of excess sample does result not only in contamination of the source but also in slow pumpout of residual materials between components and thus background. Contamination via the desorption from the separator is also possible.

V. Silylation of G.C. Components and Interface

Since thermal reactions are partly due to catalytic activity of a small number of sites, silylation of chromatographic components has become a very popular method for decreasing such reactivity. The technique can easily be applied to interfaced parts and the choices and uses of silanizing reagents can be referred to in the technical literature from Pierce Chemical Company (37). In our work occasional silanization maintained performance of the separator, column and interface lines.

VI. Resolution and Mass Range of Mass Spectrometer

For most of G.C./M.S. work, medium-low resolution ($\sim$1000) is apparently satisfactory. Medium resolution ($\sim$3000) does not offer any advantage, while high resolution G.C./M.S. is only used in special cases and then needs the aid of a computer. Only low resolution ($\sim$1000) was employed for this work and nominal mass is marked by reference compound PFK in another beam. This is the merit of a double-beam mass spectrometer.

The mass range of AEI-MS-30 is limited by accelerating

voltage which is usually set at 4KV. and has a practical range from m/e = 675 down to m/e = 2. The mass range can be expanded up to m/e = 1300 using 2 KV. The relative sensitivity is therefore reduced and not particularly recommended in our work. However, use of the peak matching decades in a static mode permits selection of an upper mass range from m/e = 600 to m/e = 900 and relatively little sensitivity is lost. This is not carried out for every run unless required, because too much paper will be wasted on scans from high to low mass. Furthermore, the understanding of the history of the sample analyzed provides the choice of upper mass of each scan and this is also considered to be advantageous for saving paper.

VII. Scan Rate

Without the problem of amplifier and recorder frequency response, there must be a compromise between scan rate, resolution and sensitivity. Once the resolution is selected and sensitivity is not an important factor, the scan rate is required to be as fast as possible. Slow scans can distort the mass spectral quality severely due to changing sample concentration during the elution of chromatographic peaks. Fig. 3 shows the distortion that occurs in the mass spectral pattern of a chromatographic peak. On the other hand, if the spectra are scanned very quickly, the change in sample concentration during the scan is insignificant, thus less distortion.

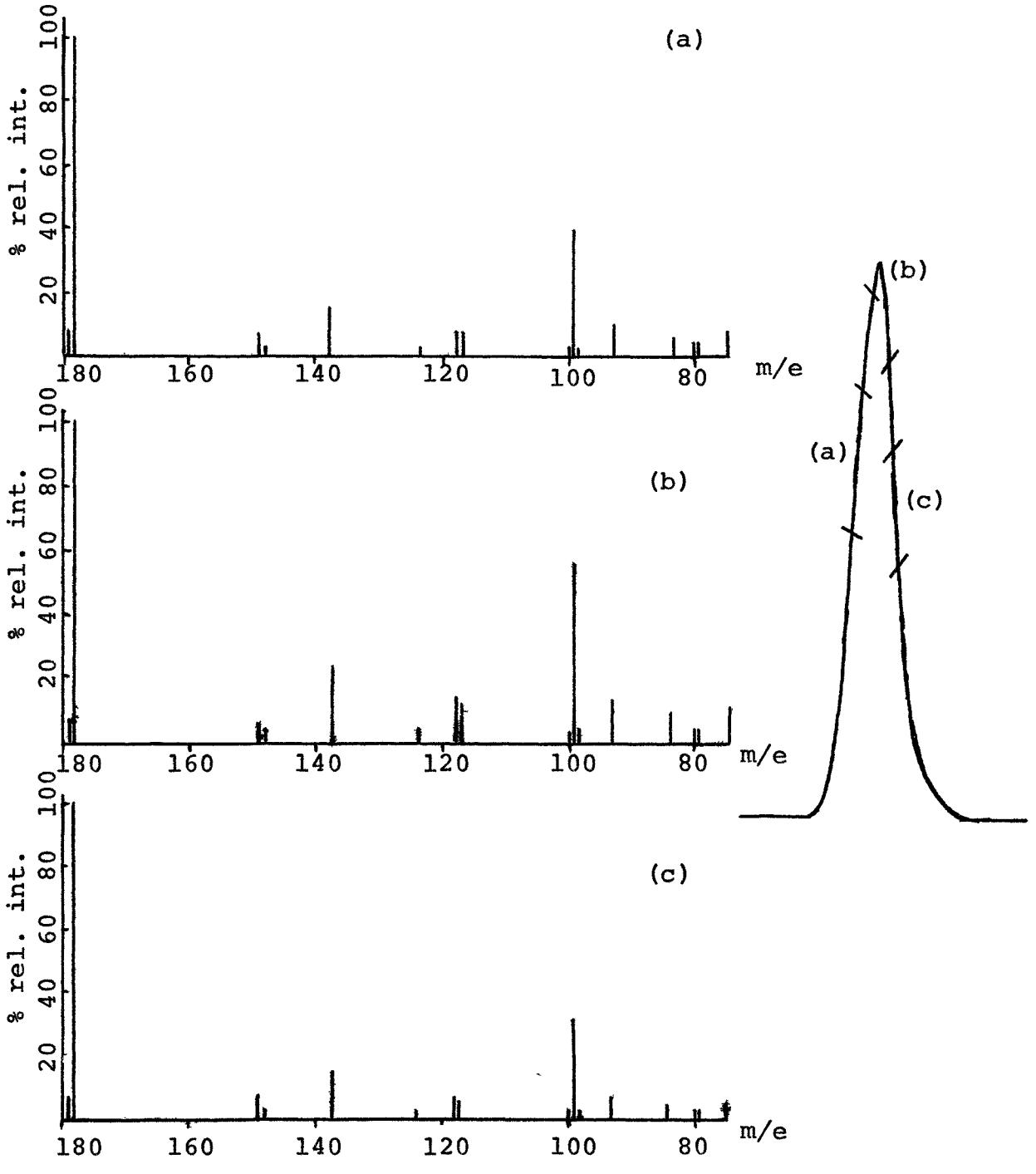


Fig. 3. Distortion of the mass spectrum of pentafluorobenzene due to the variation of concentration that occurs while scanning a chromatographic peak. (a) Scanning up the peak. (b) Scanning across the top. (c) Scanning down the peak.

VIII. Interpretation and Confirmation of Mass Spectra

It is possible to use the mass spectra to check when unseparated G.C. peaks are suspected. Fig. 4 shows how two unseparated components in one G.C. peak are easily pointed out. On the other hand the classical weakness of mass spectrometry for the identification of isomers is still present and this is primarily due to the similarities of mass spectra of isomers. To analyze a synthetic mixture, the deduction of most probable reaction pathways might aid in the speculation of the structures of such isomers. As usual, the molecular ion is of most importance. The halogen-containing compounds have characteristic isotopic patterns and thus elemental composition is easily determined using isotopic abundance methods. A comparison between measured and calculated isotopic pattern of $C_9H_{27}Si_5O_5^+$ is shown in Fig. 5. Further confirmation of all compounds involved has also been done wherever references are accessible.

In conclusion a complete gas chromatogram and several associated mass spectra are given in Fig. 6 to illustrate the ease of identification for G.C. peaks by mass spectra. It is no wonder that G.C./M.S. method is a promising technique for quickly monitoring and identifying synthetic mixtures. Although the extremely high initial and operating cost may limit its use, this is significantly compensated for by the requirement of small sample and many other potential applications.

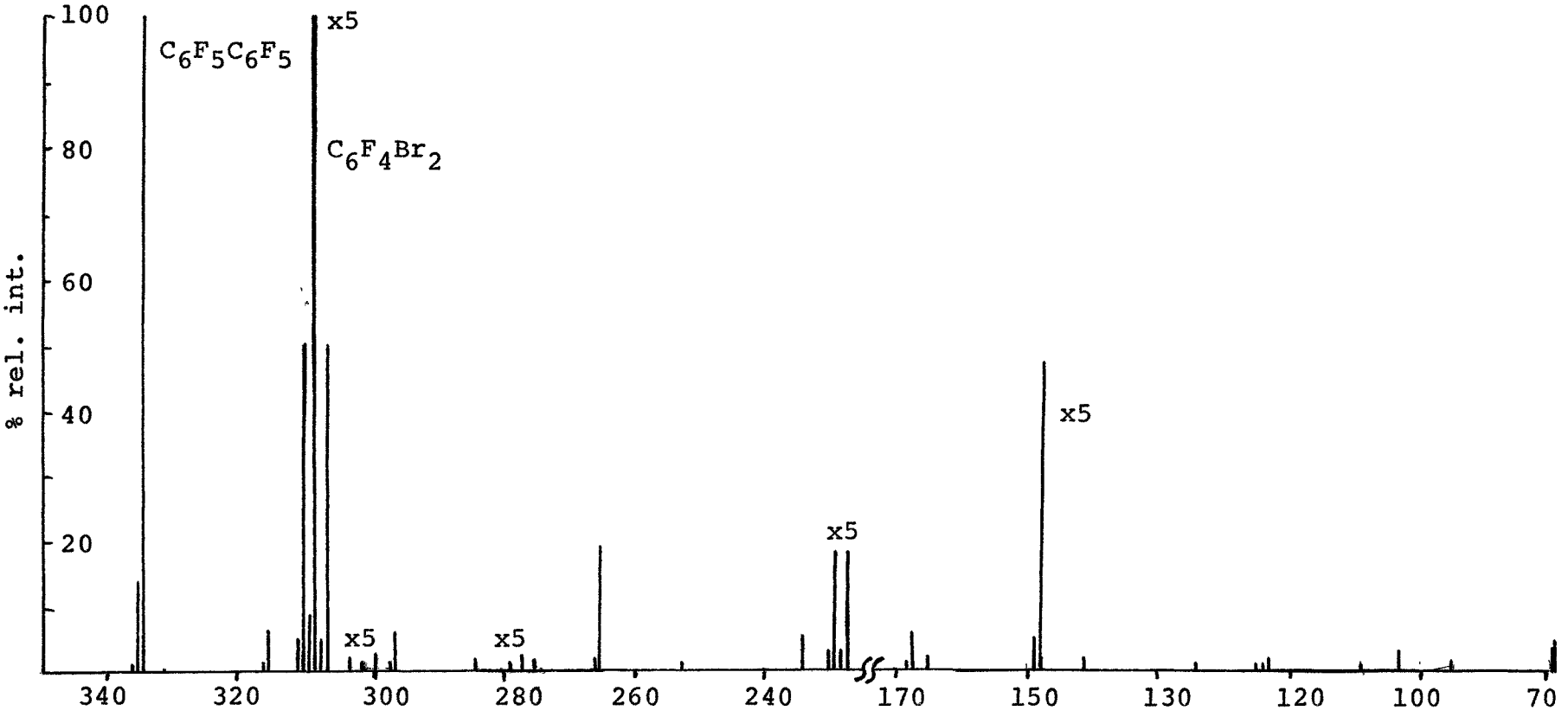


Fig. 4. Mass spectra obtained from one unseparated G.C. peak are identified to contain C_6F_5-C_6F_5 and $C_6F_4Br_2$.

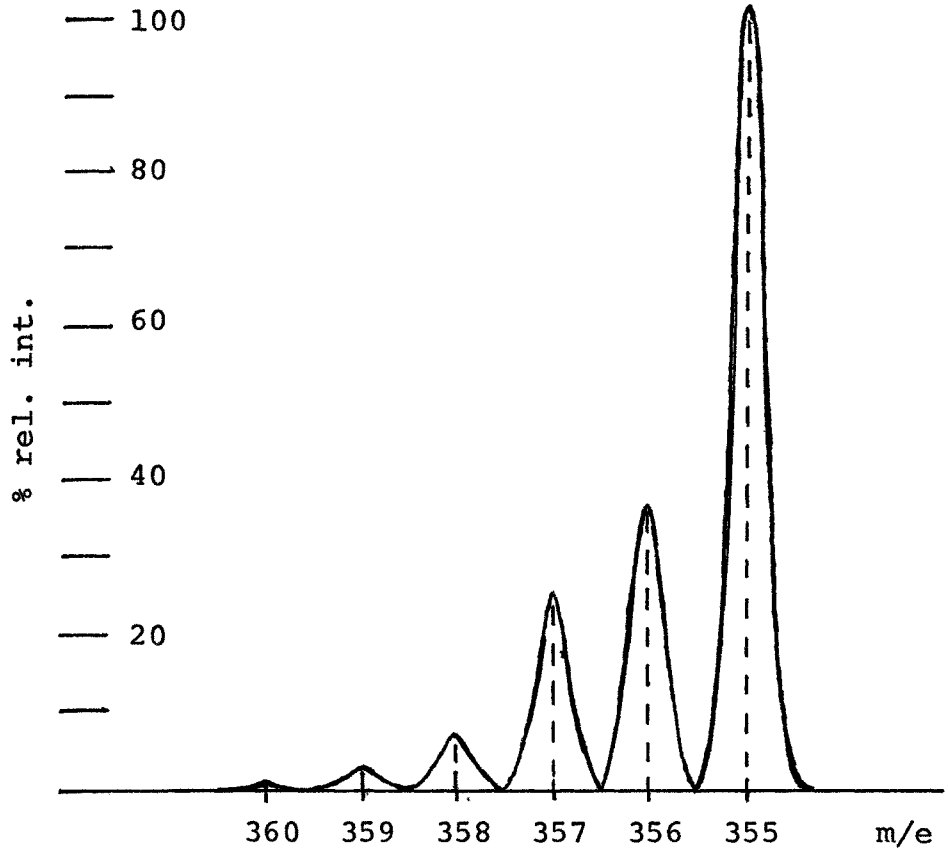
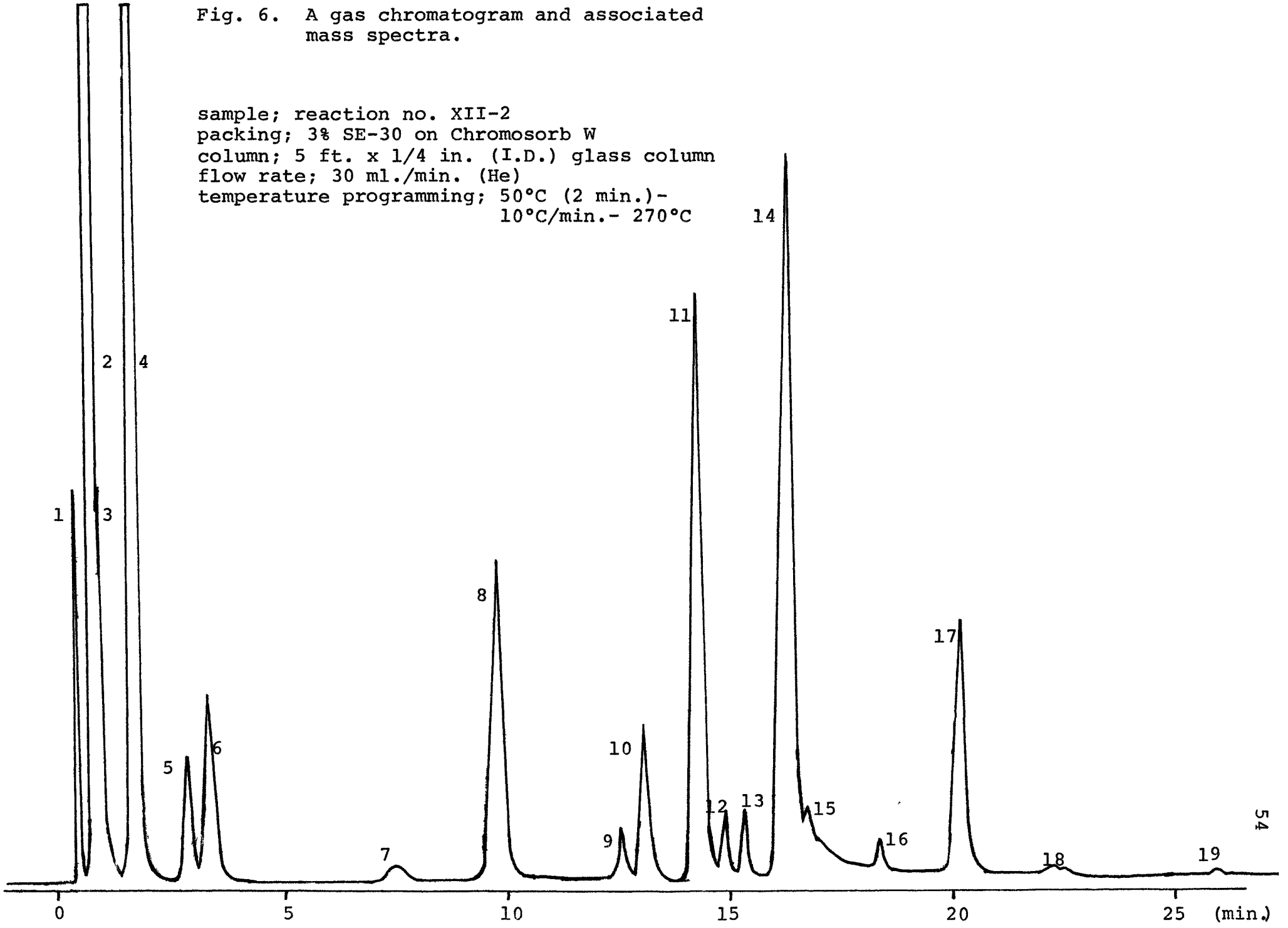
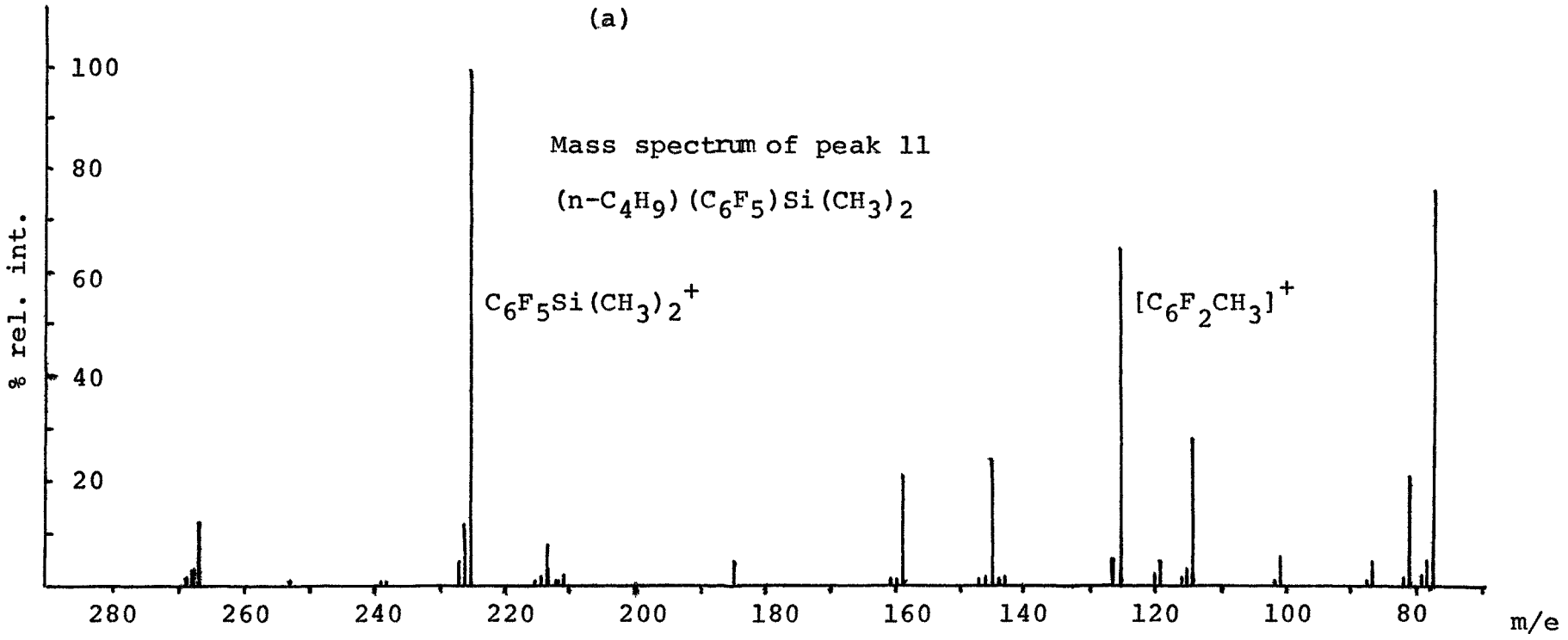
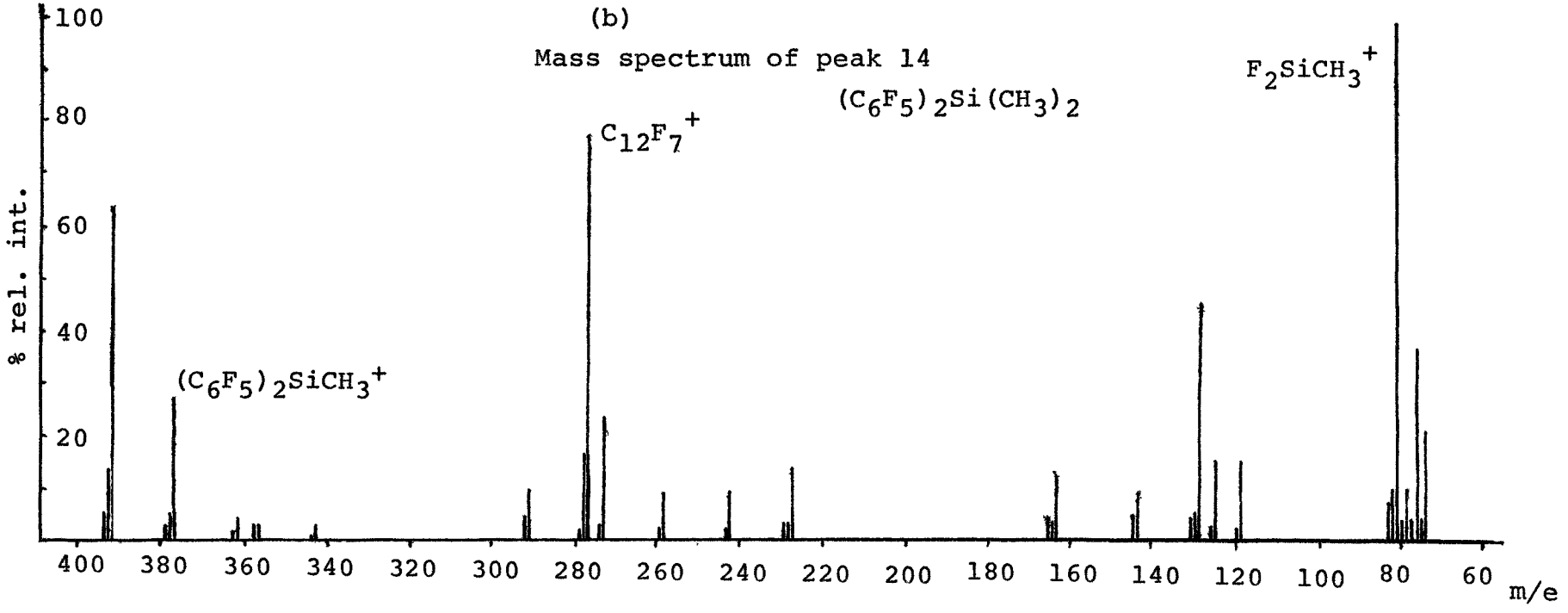


Fig. 5. Isotopic abundance of $C_9H_{27}Si_5O_5^+$ ion.
(i) measured; curve line
(ii) calculated; dotted line

Fig. 6. A gas chromatogram and associated mass spectra.



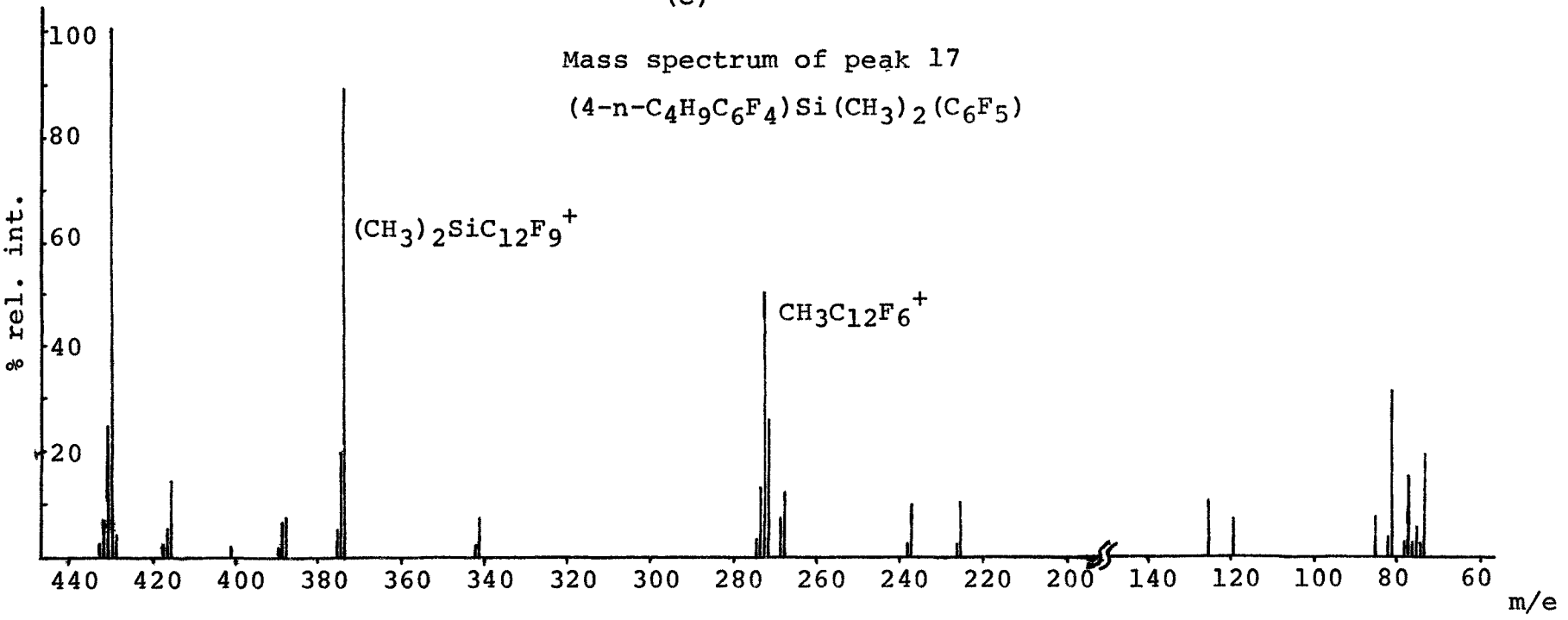

(a)
Mass spectrum of peak 11
(n-C4H9)(C6F5)Si(CH3)2
C6F5Si(CH3)2+
[C6F2CH3]+
% rel. int.
100
80
60
40
20
280
260
240
220
200
180
160
140
120
100
80
m/e


(b)
Mass spectrum of peak 14
(C6F5)2Si(CH3)2
C12F7+
F2SiCH3+
(C6F5)2SiCH3+
% rel. int.
100
80
60
40
20
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
m/e

(c)

Mass spectrum of peak 17

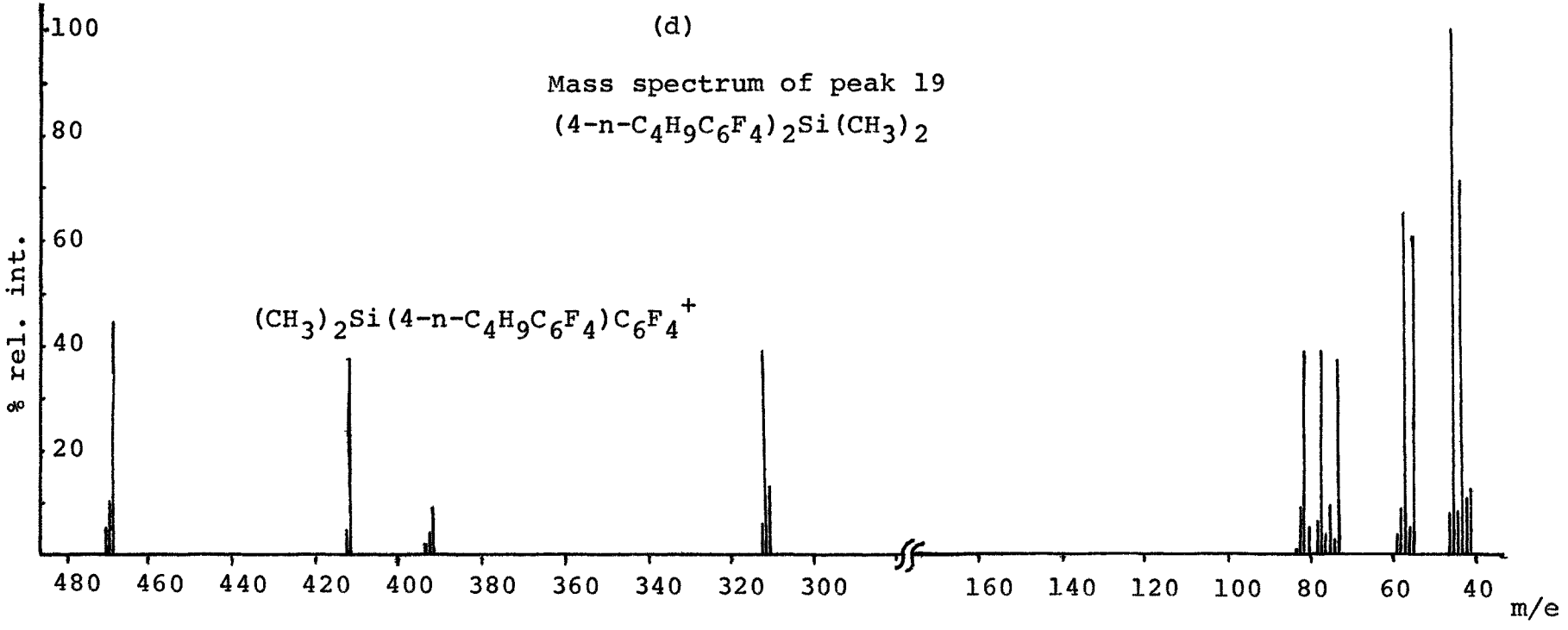
$(4\text{-n-}C_4H_9C_6F_4)Si(CH_3)_2(C_6F_5)$



(d)

Mass spectrum of peak 19

$(4\text{-n-}C_4H_9C_6F_4)_2Si(CH_3)_2$



2. Reactions of Pentafluorophenyl Derivatives

That the nature of scientific work does change due to the advent of more delicate, sensitive instruments is not unusual any more and this is especially true for the analysis of trace compounds in the analytical field. Since our concern also includes the many trace products produced during the course of reaction, attempts were made to avoid doing the comparison as to why a particular trace product was detected in one reaction, but not in the other similar reaction, and to avoid errors due to the sampling procedures. Instead several interesting phenomena observed in the reactions under the conditions used are discussed, and their reaction pathways are postulated. For a few products which to our knowledge are not yet reported, the possibilities of scale-up are predicted and the designs of new reactions are suggested.

In the following reactions our achievements, so far, in the investigation of substitution, reactivity and mechanism of reactions of pentafluorophenyl derivatives is briefly assessed and the results of our work discussed.

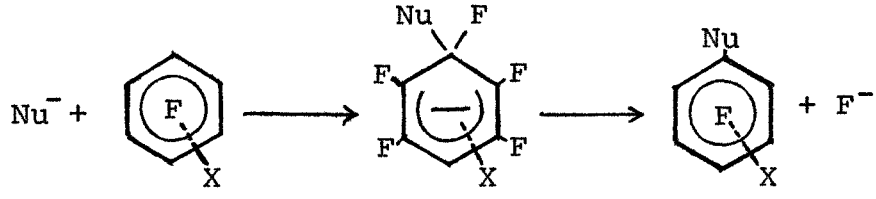
I. Substitution, Reactivity and Mechanism

In most cases, for substitution in C_6F_5X derivatives the main product arises from displacement of a fluorine atom para to the substituent group X (for example, where X = H, CH_3, CF_3, NO_2, C_6F_5, etc.). In a few cases (X = NH_2, O^-) meta replacement predominates while for (X = OCH_3, $NHCH_3$), comparable amounts of meta and para replacement occur (37, 38).

The effect of substituents on rate is, however, in the direction expected for a nucleophilic aromatic substitution; electron-donating groups deactivate while electron-withdrawing groups activate.

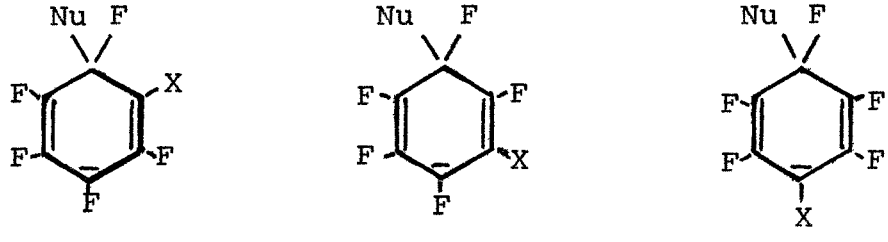
As in electrophilic substitution in benzene derivatives there is a very wide spread in rates, but one very contrasting feature is that the pattern of substitution is relatively insensitive to the substituent.

A mechanism involving the intermediate σ-complex (A) which is believed to be formed (as in many S_NAr reactions (39) in the rate-determining steps) and to provide a good model for the transition states involved (2), is assumed.



(A)

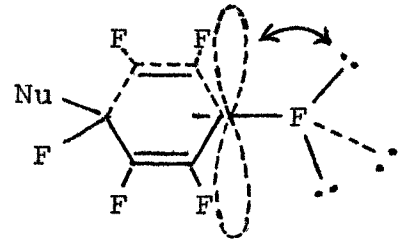
Furthermore, in order to account for the unusual orientation of substitution in reactions of pentafluorophenyl derivatives the para-quinonoid (B) canonical structures are also assumed to be major contributors (38).



(B_1) (B_2) (B_3)

ortho-substitution meta-substitution para-substitution

Since the canonical structures (B_1) and (B_2) are strongly carbanion destabilizing due to the coulombic repulsion between π -electrons and fluorine lone-pair electrons (C), the para-substitution



(C)

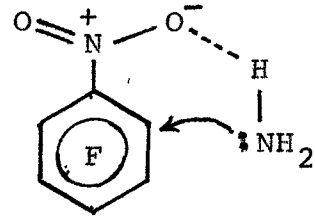
involving the intermediate (B_3) predominates in such reaction systems. On the other hand, when the substituent X is NH_2 or O^-, (C) is more important and this does explain why the nucleophile enters meta to the substituent.

The simple generalization has equally been applicable for benzenoid systems that an entering nucleophile avoids attack at positions which are para to a fluorine (2) and the position of attack in a number of systems (9) appears to support this.

This view has currently been accepted, although it has also been disputed for grossly exaggerating the deactivating influence of a para fluorine and underestimating the importance of activation by fluorine at positions ortho to the point of attack (activation by polarization of the ground state) (40).

There are a few special cases of preferred ortho attack, exemplified in the reaction of pentafluoronitrobenzene with NH_3. This is attributed to hydrogen-bonding (D) of

the nucleophile to the nitro group leading to a low-energy transition state for ortho than para substitution.



(D)

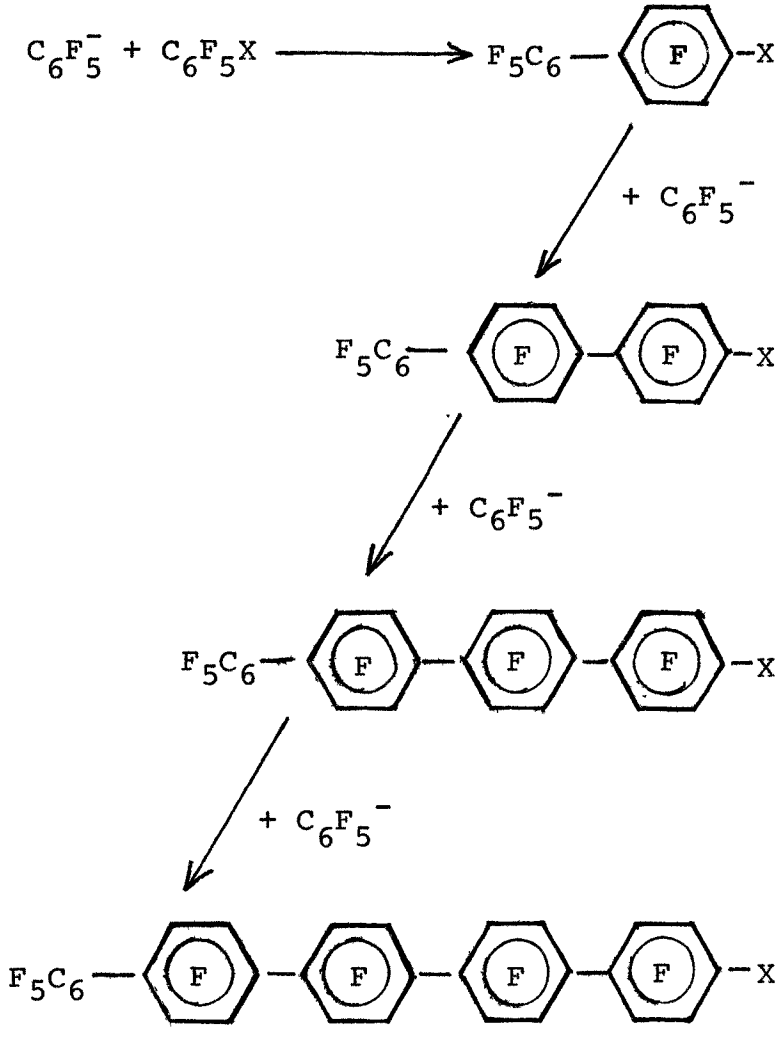
II. Reactions of Pentafluorophenyllithium

In this part as the same type of reaction takes place in each case, the common reaction feature is mentioned first and then several interesting results are pointed out for further discussion.

Early in the preparation of pentafluorophenyllithium, Tatlow et al. (3) have studied the stability of this organometallic under certain temperature conditions and Tamborski et al. (41) expanded the study to include various solvents as well as temperatures. The consistent conclusions from two independent works have been made that pentafluorophenyllithium is more stable in ether than in tetrahydrofuran, while decomposition occurs at higher temperature, but an appreciable amount exists for a reasonable time (ca. 1 hour) at room temperature.

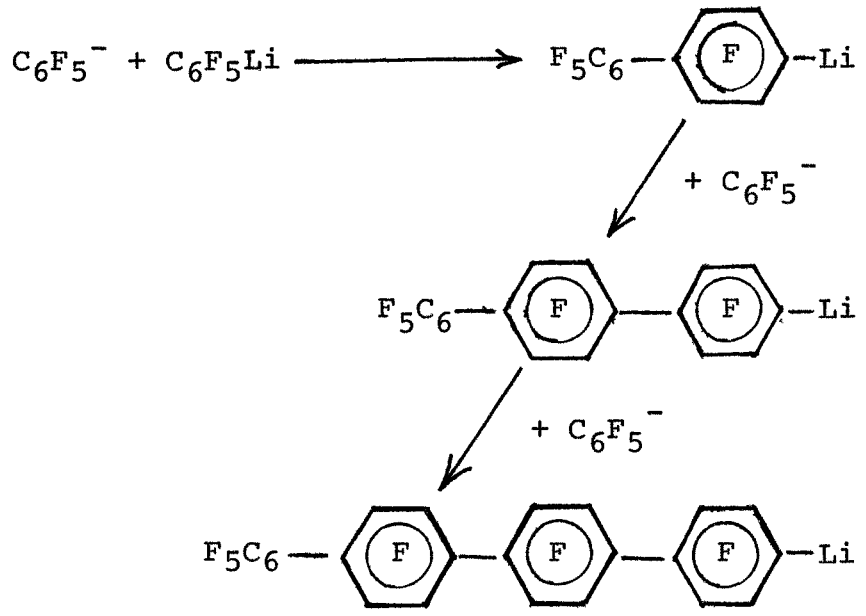
Since we are attempting no particular syntheses in our reactions and are using a highly sensitive G.C./M.S. method, the reaction temperature is varied while ether is the only solvent used. In doing so, it is apparent that two reaction

types have taken place; first, as mentioned earlier, pentafluorophenyl anion acts as a nucleophile and attacks pentafluorophenyl derivatives, C_6F_5X (X = H, F, Cl, Br, I) at para-position to yield $C_6F_5(C_6F_4)_nC_6F_5X$. This is shown schematically in A.

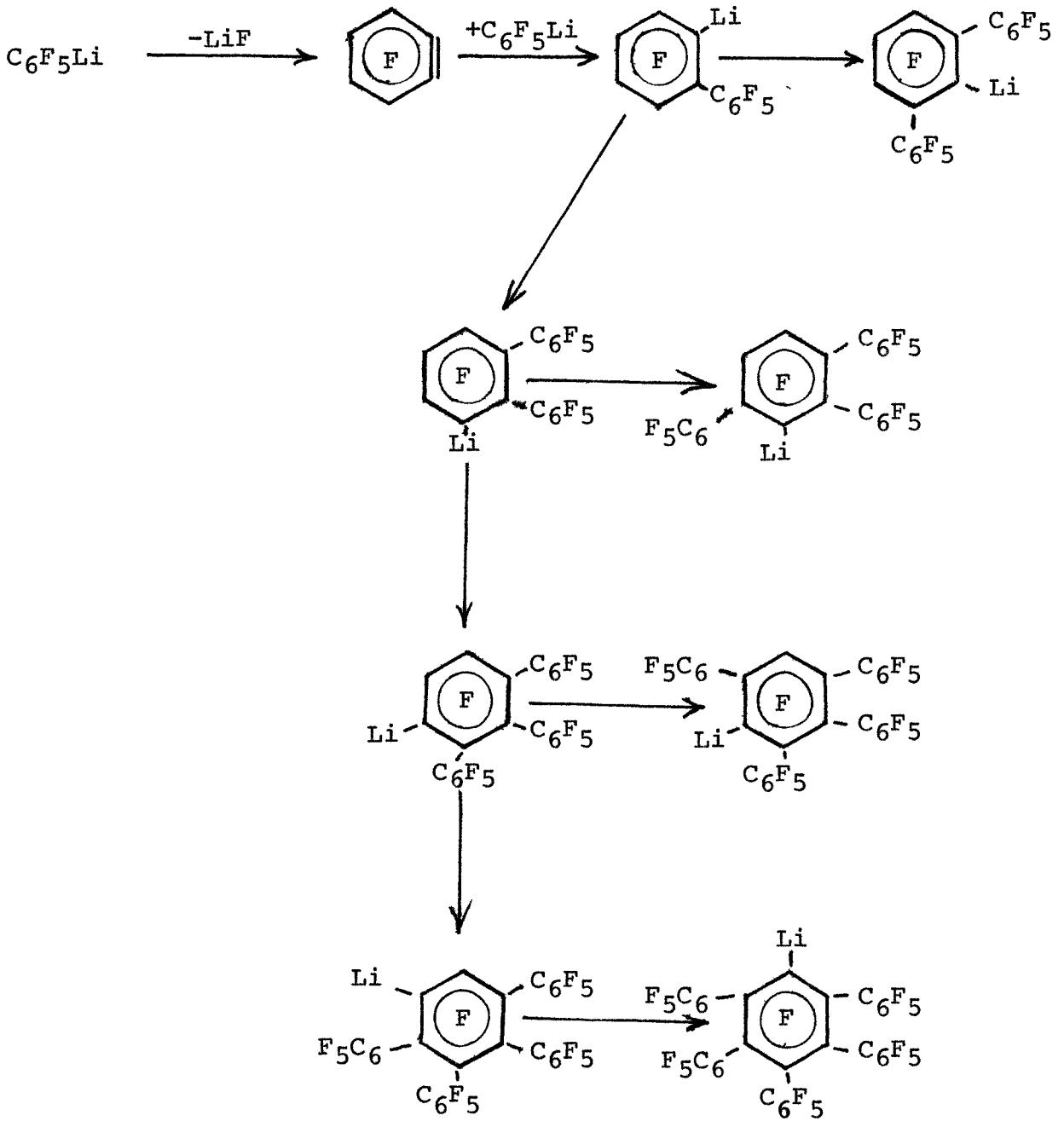


, etc. Scheme A

Another scheme B which would yield the similar result can also be presumed.



In the case of C_6F_5X (X = H, Br, I), Li/X exchange can occur in each step, while for X = F, Cl, exchange is believed not to take place, all organolithiums will yield hydrolysis products during the work-up procedure. Both schemes above involved the elimination via the intermolecular loss of lithium fluoride. Secondly, a high temperature favored reaction type occurs via the intramolecular loss of lithium fluoride to form an extremely bond-deformed reactive fluorobenzyne intermediate. This is shown schematically in C.

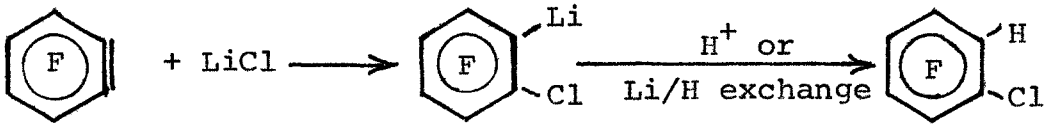


Scheme C

where in each species Li/X exchange could take place when X is H, Br, I and the proper source is available. These intermediates might survive till hydrolysis is carried out if no exchange or other reaction takes place.

Another feature which is observed only to a small extent, and is mainly due to lesser amounts of reactants available, is the addition of LiX (X = H, Cl, Br, I) to fluorobenzyne, followed by exchange for X = H, Br, I and/or hydrolysis. The solubilities of LiX (X = H, F, Cl, Br, I) in ether/hexane apparently follows the order LiH $\approx$ LiI $>$ LiBr $>$ LiCl $>$ LiF and the electronegativities of X explains this properly. Therefore the ease of addition to fluorobenzyne may be expected to follow this order. This phenomenon is consistent with the observation by Tatlow et al. (11) who treated tetrafluorobenzyne with LiX (X = Cl, Br, I). As mentioned earlier, the addition of pentafluorophenyllithium to tetrafluorobenzyne offers the route for the preparation of 2-$XC_6F_4C_6F_5$ (X = H, Br, I), and the ease of the addition of LiX (X = H, Br, I) to tetrafluorobenzyne is apparent but if it is a good route for the preparation of 1,2-dihydro-, 1,2-hydro-halo- or 1,2-dihalo-tetrafluorobenzene is questionable because of the sparing solubilities of these salts in organic solvents. Perhaps the recent development of phase-transfer reaction (43) will cast some light on this.

In Table-5, traces of $C_{6n}H_{4n}HCl$ (n = 1, 2, 3) observed show that reactions between LiCl (produced from the reaction of C_6F_5Li with $(CH_3)_3SiCl$) and tetrafluorobenzyne, 1-pentafluorophenyl-2,3,4-trifluorobenzyne and 1,2-bis(pentafluorophenyl)-3,4-difluorobenzyne, respectively, have taken place, and this can be exemplified.



Whether the mode of addition is stepwise or four-center addition, as in the case of pentafluorophenyllithium is still unclear.

In Table-6, traces of $C_{6n}F_{4n}H_2$ (n = 1∼4) may be explained in terms of the addition of LiH to corresponding fluorobenzyne. The source of LiH may derive from the coupling reaction of n-C_4H_9Li with n-C_4H_{10}, which is the product of the exchange reaction between pentafluorobenzene and n-C_4H_9Li and the observation of some n-octane may be evidence for this coupling. In the C_6F_6-C_6F_5Li system, part of C_6F_6 is recovered while $C_{6n}F_{5n}$ (n = 2∼4) shows the attack via C_6F_5 anion has occurred. It is interesting to note that an appreciable amount of $C_6F_5(n\text{-}C_4H_9)$ and $C_6F_4(n\text{-}C_4H_9)_2$ is also detected. In view of the susceptibility of C_6F_6 to the attack of n-C_4H_9Li (44), it may be speculated the reverse reaction takes place after the addition of C_6F_6 in spite of the presence of the suspected excess of n-C_4H_9Li.

$$C_6F_5H + n\text{-}C_4H_9Li \rightleftharpoons C_6F_5Li + n\text{-}C_4H_{10}$$

$$C_6F_6 + n\text{-}C_4H_9Li \longrightarrow C_6F_5(n\text{-}C_4H_9) + LiF$$

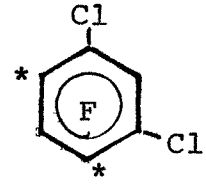
In the C_6F_5Li - C_6F_5Cl system, most of C_6F_5Cl is recovered but the G.C. separable isomers of $C_{6n}F_{4n+1}Cl$, for example two isomers for $C_6F_5C_6F_4Cl$, may lead to the speculation that either the substitution of C_6F_5 group for F has occurred at both para and ortho positions or one isomer formed by way of substitution while another via Li/Cl exchange. Although it is claimed Li/Cl exchange does not take place (15), our observation is made with more sensitive instrumentation and the result discussed later further supports our speculation. In the C_6F_5Li - C_6F_5Br system, $C_{6n}F_{4n}Br_2$ (n = 1$\sim$3) can be explained to be from the addition of LiBr to corresponding fluorobenzynes, then followed by exchange, while LiBr is formed from the coupling of n-C_4H_9Li with n-C_4H_9Br; the same is observed for the C_6F_5Li - C_6F_5I system, but LiI comes from the reaction of n-C_4H_9Li with n-C_4H_9I. In the C_6F_5Li - C_6H_6 system, as there was difficulty in getting the products through G.C./M.S., the only two main products are tetrafluorobenzobicyclo[2,2,2]octatriene and 1-pentafluorophenyl-2,3,4-trifluorobenzobicyclo[2,2,2]octatriene. It is likely that both are from the addition of benzene to corresponding fluorobenzynes by way of 1,4-addition.

In Table-7, in the presence of n-C_4H_9Br, no difference is observed compared to a series without it and this is quite understanble because the following reaction equilibrium is towards the right side.

$$C_6F_5Br + n\text{-}C_4H_9Li \rightleftharpoons C_6F_5Li + n\text{-}C_4H_9Br$$

Therefore the presence of $n\text{-}C_4H_9Br$ is expected to have little effect.

In Table-8, most of the starting materials are recovered while $C_{6n}F_{4n}H_2$ (n=2 ~ 4) in $C_6F_4H_2$ - C_6F_5Li system, $C_{6n}F_{4n}Cl_2$ (n = 2 , 3) in $C_6F_4Cl_2$ - C_6F_5Li system and $C_{6n}F_{4n-1}Cl_3$ (n = 2~4) in $C_6F_3Cl_3$ - C_6F_5Li system provides apparent evidence that the replacement by C_6F_5 groups of F atoms actually takes place and the favored substitution, as mentioned earlier, can be presumed as follows (location of charge)



As for $1,3,5\text{-}C_6F_3Cl_3$, three F atoms have the equal chances to be replaced by C_6F_5 group. The observation of $C_{6n}F_{4n+1}Cl$ (n = 2 4) in $C_6F_4Cl_2$ and $C_6F_3Cl_3$ systems strongly indicates Li/Cl exchange does occur, but to a much lesser extent compared to the cases of X = I, Br, H.

It is interesting to see the role, if any, of low-energy d orbitals of pentafluorophenyl organometallics in the transition state, therefore $C_6F_5Si(CH_3)_3$, $(C_6F_5)_3P$, and $(C_6F_5)_3P{=}O$ are submitted to the attack of a nucleophile, the C_6F_5 anion, the corresponding hydrogen-analogues, which would seem to be less susceptible to the attack of

nucleophile, being examined for the purpose of comparison.

The results in Table-9 show that not even a trace amount of the products anticipated is detected, but the observation of traces of $n\text{-}C_4H_9C_6F_4Si(CH_3)_3$ which may be due to excess of $n\text{-}C_4H_9Li$ and will be discussed later suggests that it may be helpful if the reaction is carried out without scheme C competing. We are unable to determine if $Si\text{-}C_6F_5$ or $Si\text{-}C_6H_5$ bond cleavage by C_6F_5Li also takes place.

The results in Table-10, for the C_6F_5Li - $(C_6F_5)_3P$ system, show that C_6F_5 anions have probably replaced F atoms to form $(C_6F_5)_2(C_{12}F_9)P$, $(C_6F_5)(C_{12}F_9)_2P$, and $(C_{12}F_9)_3P$. Provided this is true, the 3d-orbital of phosphorus atom might be considered as having been involved in the transition state. But another possibility that for example, $(C_6F_5)_2(C_{12}F_9)P$ can probably be formed via the group exchange between $(C_6F_5)_3P$ and $C_{12}F_9Li$ should also be considered. This may apparently be predicted from the stabilities of $(C_6F_5)_3P$ and $(C_6F_5)_2(C_{12}F_9)P$ but it is really unfortunate that such products are not yet reported. In view of the report (17) that the pattern of substitution of pentafluorophenyl phosphorus is very sensitive to solvent used, it seems to be unwise to speculate this without the support of more spectroscopic data. This sort of problem might be understood from further work in this lab.

In the C_6F_5Li - $(C_6F_5)_3P{=}O$ system the detection of $(C_6F_5)_3P$ and $(C_6F_5)_2(C_{12}F_9)P$ may be attributed to the

presence of impurity $(C_6F_5)_3P$. As to whether or not $(C_6F_5)_3P{=}O$ has been reduced by some sort of reducing reagent in the solution first and then further reaction followed, further study would be required.

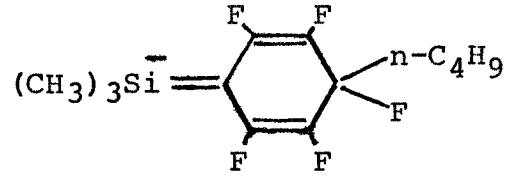
Ferrocene, $(\pi\text{-}C_5H_5)_2Fe$, is extremely susceptible to the attack of electrophiles and only accessible to nucleophiles in a few particular systems according to the reports so far. Its reaction with fluoroaromatic compounds was reported by Rosenberg in his patent (45) which treated lithioferrocene with hexafluorobenzene. In the results shown in Table-11, as might be expected, no substitution is detected, but traces of $(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4C_6F_4H)Fe$ indicates $(\pi\text{-}C_5H_5)_2Fe$ has been lithiated by either excess of $n\text{-}C_4H_9Li$ or C_6F_5Li (unlikely) and then two pathways followed to yield this product; by way of (i) the attack of $(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4Li)Fe$ on C_6F_5H (ii) the addition of $(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4Li)Fe$ to tetrafluorobenzyne, then followed by Li/H exchange or hydrolysis. In view of the report by Rosevear et al. (46) who treated C_6F_5Br with lithioferrocene and obtained only products via Li/Br exchange, it is apparent that route (ii) is favored because Li/H exchange may also proceed easily. Therefore it may be expected that if lithioferrocene is added to tetrafluorobenzyne, $(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4C_6F_4H)Fe$ and to a lesser extent, $(\pi\text{-}C_5H_4C_6F_4H)_2Fe$ can be formed.

III. Reactions of $(C_6F_5)_nSi(CH_3)_{4-n}$, (n = 1, 2)

No particular products via exchange between pentafluorophenyl derivative and salts, even traces, are detected even at higher temperature. $(C_6F_5)_nSi(CH_3)_{4-n}$, (n = 1, 2), are the major products in each case. Similar to the reactions of pentafluorophenyllithium, traces of $C_6F_4Br_2$, C_6F_4BrH, and $C_6F_3Br_2H$ are formed since small amounts of Grignard, C_6F_5MgBr, have decomposed to form tetrafluorobenzyne at room temperature. Thus the salt MgBrCl adds to it, finally followed by exchange or hydrolysis.

In Table-1 and -2, the detection of $(C_6F_5)_2$ may be due to the coupling between C_6F_5MgBr and C_6F_5Br, while $(CH_3)_3SiOSi(CH_3)_3$ is the product of acid-catalyzed hydrolysis and dehydration of excess $(CH_3)_3SiCl$. The same procedure as above can lead $(CH_3)_2SiCl_2$ to yield a series of cyclic siloxanes, $((CH_3)_2SiO)_n$ n = 3$\sim$12 and these are indeed observed in Table-2 and -4, respectively.

In Table-4, the reaction no. XII-2 shows two interesting products, $(n\text{-}C_4H_9C_6F_4)(C_6F_5)Si(CH_3)_2$ and $(n\text{-}C_4H_9C_6F_4)_2Si(CH_3)_2$, and these might be derived from the attack of excess $n\text{-}C_4H_9Li$ on $(C_6F_5)_2Si(CH_3)_2$. If the reaction of $(C_6F_5)Si(CH_3)_3$ with $n\text{-}C_4H_9Li$ is reviewed (19), it is not surprising and the transition state involving d-orbital of silicon as (E) can be assumed.



(E)

At the same time, para-substitution might be postulated because of the similarity and $(C_6F_5)_2Si(CH_3)_2$ can be treated with $n\text{-}C_4H_9Li$ directly to scale it up for further studies.

$C_6F_5Si(CH_3)_2(n\text{-}C_4H_9)$ in Table-4 shows that not only C_6F_5Li but also an excess of $n\text{-}C_4H_9Li$ has the chance to add to $(CH_3)_2SiCl_2$. But the fact that the organolithium such as $n\text{-}C_4H_9Li$ is a good cleavage reagent for organometallics should not be forgotten. Thus this product may be attributed to the cleavage of $(C_6F_5)_2Si(CH_3)_2$ by $n\text{-}C_4H_9Li$.

In Table-2, a series of products, $C_6F_5((CH_3)_2SiO)_nSi(CH_3)_2C_6F_5$, is observed and this can be added to the report by Gilman et al. (47) who directly treated $Cl((CH_3)_2SiO)_nSi(CH_3)_2Cl$ (n = 1, 2) with C_6F_5Li respectively to attain $C_6F_5((CH_3)_2SiO)_nSi(CH_3)_2C_6F_5$ (n = 1, 2).

Summary

Unexpected results often provide incentive for further study. Unexpected traces of side products which are generally neglected due to the difficulty of detection may offer routes to new compounds. G.C./M.S. techniques characterized by the speed and specificity often make the detection of such trace products possible. These are best represented by some examples selected from this work:

(i) observations of $(n\text{-}C_4H_9C_6F_4)\ (C_6F_5)Si(CH_3)_2$, $(n\text{-}C_4H_9C_6F_4)_2Si(CH_3)_2$, and $(C_{12}F_9)_{3-n}(C_6F_5)_nP$, n = 0,1,2, may strongly suggest the possibilities of the replacements of fluorine by other suitable nucleophiles on either $(C_6F_5)_2Si(CH_3)_2$ or $(C_6F_5)_3P$.

(ii) C_6F_4HX (X = Cl, Br, I), $(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4C_6F_4H)Fe$, etc. may show that other inorganic salts or organometal compounds are capable of adding to fluorobenzyne.

As for G.C./M.S. techniques, it is hard to predict its future owing to rapidly scientific progress. However, it is certain that in years ahead it would still play an important role in the analytical field as long as complicated mixtures require study.

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APPENDIX

Mass Spectral Data

NOTES: (a) Ion intensities are recorded as % of base peak = 100.

(b) Low mass cut off is at m/e = 50 except the first eleven compounds.

(c) The spectra of compounds with * signs are either poor or seriously overlapped so that only parent ion and some observed losses are noted.

Index of Partial Mass Spectra
(Ordered by molecular weight)

Mol.wt.	Spectrum no.	Mol.wt.	Spectrum no.	Mol.wt.	Spectrum no.
74	1	278	21,81	468	25
78	2	282	22	480	48
86	3	294	73	482	43
88	4	296	15	498	51
92	5	298	29	502	79
112	6	306	69	514	56
114	7	316	33	518	18
136	8	332	47	524	63
146	9,12	334	42,88	530	59
150	19,28	350	50	532	82
156	10	354	78	540	27
162	13	366	55	542	66
168	32	370	16	548	83
184	11,46	374	38	550	77
186	41,87	376	62	590	75
202	49	382	58	594	31
218	54	392	23	602	71
222	14	394	65	612	35
224	39	402	76	630	44
226	37	430	24	646	52
228	61	442	74	678	60
234	57	444	17	680	84
240	20	446	30	690	67
246	64	454	70	760	36
262	40,80	464	34	776	45
276	72	466	26	794	53
				828	85
				838	68
				976	86

Compound No.	M.W.	Parent ion int.	Mass to charge ratio								Intensities								Formula
			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	
1	74		31	29	59	45	74	27	43	28	100	51	48	38	28	25	10	7	$(C_2H_5)_2O$
2	78		78	52	51	50	77	39	79	76	100	20	19	16	16	14	6	5	C_6H_6
3	86	18	57	41	43	56	42	29	27	39	100	81	78	62	51	44	41	22	$n\text{-}C_6H_{14}$
4	88		28	29	88	58	43	31	57	30	100	60	47	34	24	22	15	11	$C_4H_8O_2$
5	92		91	92	50	63	45	51	65	39	100	100	46	40	40	39	36	36	$C_6H_5CH_3$
6	112		112	77	114	51	50	74	75	56	100	56	33	20	17	7	7	5	C_6H_5Cl
7	114		43	57	41	71	85	56	29	42	100	14	11	8	8	8	7	3	$n\text{-}C_8H_{18}$
8	136	12	57	41	21	27	39	56	28	55	100	76	50	35	23	22	17	15	$n\text{-}C_4H_9Br$
9	146		146	148	111	75	50	113	74	150	100	62	41	29	17	13	10	9	$o\text{-}C_6H_4Cl_2$
10	156		77	156	158	51	50	38	74	78	100	90	88	15	9	7	7	5	C_6H_5Br
11	184		57	184	29	41	27	39	127	28	100	45	39	36	21	10	8	6	$n\text{-}C_4H_9I$
12	146	0.00	131	75	73	103	87	45	132	59	100	95	45	22	13	13	10	8	$(n\text{-}C_4H_9O)Si(CH_3)_3$
13	162	0.00	147	148	149	73	131	59	133	117	100	17	9	9	7	4	2	2	$((CH_3)_3Si)_2O$
14	222	0.00	207	96.5	208	209	191	133	97	177	100	23	21	11	8	8	4	3	$((CH_3)_2SiO)_3$
15	296	0.00	281	282	283	133	73	265	207	191	100	29	18	10	9	8	6	6	$((CH_3)_2SiO)_4$

Compound No.	M.W.	Parent ion int.	Mass to charge ratio								Intensities								Formula
			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	
16	370	0.00	355	73	267	356	357	339	268	358	100	91	59	36	27	18	18	14	$((CH_3)_2SiO)_5$
17	444	0.00	77	341	429	147	342	430	431	325	100	94	66	34	33	30	25	22	$((CH_3)_2SiO)_6$
18	518	0.00	73	281	147	225	341	503	415	282	100	86	64	61	50	36	36	36	$((CH_3)_2SiO)_7$
19	150		135	136	150	105	137	107	119	73	100	10	8	7	4	4	3	3	$C_6H_5Si(CH_3)_3$
20	240		225	77	125	81	75	159	240	63	100	86	72	44	32	22	19	19	$C_6F_5Si(CH_3)_3$
21	278		80	278	77	222	101	81	263	155	100	28	15	10	10	9	8	6	$(n\text{-}C_4H_9C_6F_4)Si(CH_3)_3$
22	282	0.00	225	77	125	114	145	159	81	267	100	71	65	28	23	21	19	13	$(C_6F_5)Si(n\text{-}C_4H_9)(CH_3)_2$
23	392		81	277	392	129	77	377	273	75	100	77	63	43	37	27	23	20	$(C_6F_5)_2Si(CH_3)_2$
24	430		430	373	273	81	57	431	272	374	100	89	50	32	32	26	26	20	$(n\text{-}C_4H_9C_6F_4)(C_6F_5)Si(CH_3)_2$
25	468		57	55	468	81	311	77	411	73	100	58	44	42	38	38	37	35	$(n\text{-}C_4H_9C_6F_4)_2Si(CH_3)_2$
26	466	1.0	155	77	451	159	125	303	81	452	100	62	44	44	24	21	18	15	$(C_6F_5Si(CH_3)_2)_2O$
27	540	0.00	525	73	281	229	77	377	526	233	100	90	80	80	65	50	35	35	$(C_6F_5)((CH_3)_2SiO)_2Si(CH_3)_2(C_6F_5)$
28	150		150	81	99	119	151	75	100	130	100	27	12	7	7	7	5	3	$C_6F_4H_2$
29	298		298	179	197	299	151	215	229	230	100	71	30	18	17	14	13	12	$C_{12}F_8H_2$
30	446		446	377	447	363	395	396	346	378	100	33	18	14	12	9	9	8	$C_{18}F_{12}H_2$

Compound No.	M.W.	Parent ion int.	Mass to charge ratio								Intensities								Formula
			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	
31	594		594	595	425	475	297	487	506	575	100	33	14	11	8	6	5	5	$C_{24}F_{16}H_2$
32	168		168	99	137	118	149	117	93	169	100	73	53	28	28	28	28	22	C_6F_5H
33	316		316	247	317	158	278	297	216	265	100	38	25	18	12	10	9	5	$C_{12}F_9H$
34	464		464	395	465	364	414	182	396	445	100	62	22	17	14	14	12	11	$C_{18}F_{13}H$
35	612		612	613	543	306	349	512	444	475	100	29	25	14	10	8	8	7	$C_{24}F_{17}H$
36*	760		parent ion is identified by intense doubly charged ion at m/e=380																$C_{30}F_{21}H$
37	226		226	179	200	225	207	206	161	151	100	60	47	37	37	27	20	17	$C_6F_4C_6H_6$
38	374		374	296	354	223	355	309	305	375	100	91	41	41	27	27	27	25	$C_{12}F_8C_6H_6$
39	224		181	224	182	57	163	225	164	161	100	67	51	11	9	9	6	6	$C_6F_5(n\text{-}C_4H_9)$
40	262		219	177	262	221	57	178	159	176	100	50	50	21	19	11	10	10	$C_6F_4(n\text{-}C_4H_9)_2$
41	186		186	117	31	93	155	167	136	98	100	50	28	20	15	14	10	8	C_6F_6
42	334		334	265	335	315	167	296	234	266	100	19	13	6	6	6	5	3	$C_{12}F_{10}$
43	482		482	413	483	382	413	463	432	444	100	40	28	14	11	10	8	6	$C_{18}F_{14}$
44	630		630	631	561	492	315	523	511	530	100	23	11	9	6	5	5	4	$C_{24}F_{18}$
45*	776		parent ion is identified by intense doubly charged ion at m/e=389																$C_{30}F_{22}$

Compound No.	M.W.	Parent ion int.	Mass to charge ratio								Intensities								Formula
			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	
46	184		184	186	99	149	185	115	150	187	100	36	25	20	9	7	5	5	C_6F_4HCl
47*	332		M^+, $(M-F)^+$, $(M-F_2)^+$, $(M-Cl)^+$, $(M-FCl)^+$, $(M-CF_3)^+$, $(M-CF_2Cl_1)^+$																$C_{12}F_8HCl$
48*	480		M^+, $(M-F)^+$, $(M-Cl)^+$, $(M-CF_2)^+$, $(M-FCl)^+$, $(M-CF_2Cl)^+$																$C_{18}F_{12}HCl$
49	202		202	204	117	167	133	203	93	101	100	33	22	20	8	8	5	4	C_6F_5Cl
50	350		350	352	265	296	351	179	175	281	100	41	24	20	19	13	9	8	$C_{12}F_9Cl$
51	498		498	500	499	413	444	249	501	375	100	34	19	12	9	9	7	6	$C_{18}F_{13}Cl$
52	646		646	648	647	498	323	577	500	542	100	46	35	28	18	14	13	11	$C_{24}F_{17}Cl$
53*	794		parent ion is identified by doubly charged ion at m/e=397																$C_{30}F_{21}Cl$
54	218		218	220	153	183	155	98	109	117	100	64	28	19	10	10	10	8	m-$C_6F_4Cl_2$
55	366		366	368	296	218	367	370	312	381	100	67	29	21	19	19	12	12	$C_{12}F_8Cl_2$
56*	514		M^+, $(M-Cl)^+$, $(M-2Cl)^+$, $(M-CF_3Cl)^+$, $(M-FCl_2)^+$																$C_{18}F_{12}Cl_2$
57	234		234	236	238	149	199	151	164	133	100	100	31	20	18	15	15	13	1,3,5-$C_6F_3Cl_3$
58	382		384	382	312	386	430	231	314	364	100	97	47	30	30	27	20	19	$C_{12}F_7Cl_3$
59	530		530	532	445	478	464	495	534	447	100	95	42	37	37	32	26	26	$C_{18}F_{11}Cl_3$
60*	678		identified by typical isotopic pattern of molecular ion																$C_{24}F_{15}Cl_3$

Compound No.	M.W.	Parent ion int.	Mass to charge ratio								Intensities								Formula
			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	
61	228		228	230	149	99	229	231	80	130	100	100	55	45	10	10	10	9	C_6F_4HBr
62*	376		identified by molecular ion.																$C_{12}F_8HBr$
63*	524		identified by molecular ion.																$C_{18}F_{12}HBr$
64	246		246	248	117	167	98	93	79	148	100	100	94	81	22	22	18	13	C_6F_5Br
65	394		296	265	315	394	396	247	197	198	100	100	28	19	19	19	19	19	$C_{12}F_9Br$
66	542		542	544	413	444	375	463	425	163	100	100	41	14	11	8	8	6	$C_{18}F_{13}Br$
67	690		690	692	691	693	561	523	542	592	100	100	32	32	29	19	16	14	$C_{24}F_{17}Br$
68*	838		parent ion is identified by doubly charged ion at m/e=419																$C_{30}F_{21}Br$
69	306		308	306	310	148	279	277	98	117	100	51	51	47	18	18	13	9	$C_6F_4Br_2$
70*	454		M^+, $(M-Br)^+$, $(M-Br_2)^+$, $(M-Br_2F)^+$, $(M-Br_2CF)^+$, $(M-Br_2CF_2)^+$.																$C_{12}F_8Br_2$
71	602		604	602	606	444	413	523	525	605	100	58	50	36	33	33	31	22	$C_{18}F_{12}Br_2$
72*	276		M^+, $(M-I)^+$, $(M-HI)^+$, I^+																C_6F_4HI
73	294		294	117	167	93	98	148	295	127	100	60	53	19	14	11	10	6	C_6F_5I
74	442		442	296	267	315	443	423	316	268	100	45	43	24	16	10	6	6	$C_{12}F_9I$
75	590		590	591	413	463	444	296	414	464	100	20	20	12	11	8	4	3	$C_{18}F_{13}I$

Compounds No.	M.W.	Parent ion int.	Mass to charge ratio								Intensities								Formula
			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	
76	402		402	148	98	275	117	403	129	179	100	29	11	9	6	6	3	3	$C_6F_4I_2$
77*	550		M^+, $(M-I)^+$, $(M-2I)^+$, I^+																$C_{12}F_8I_2$
78	354		354	356	148	227	229	355	357	149	100	100	57	21	21	13	13	11	C_6F_4IBr
79*	502		M^+, $(M-I)^+$, $(M-IBr)^+$																$C_{12}F_8IBr$
80	262		262	183	108	263	261	184	185	107	100	32	20	18	14	7	5	4	$(C_6H_5)_3P$
81	278		277	278	201	77	199	183	185	51	100	39	20	16	14	14	11	9	$(C_6H_5)_3P=O$
82	532		69	198	129	532	110	367	117	217	100	29	27	23	22	17	15	13	$(C_6F_5)_3P$
83	548		69	548	296	532	217	365	269	227	100	52	50	45	38	20	17	17	$(C_6F_5)_3P=O$
84	680		680	530	513	69	613	365	217	444	100	55	23	23	22	18	13	11	$(C_{12}F_9)(C_6F_5)_2P$
85*	828		parent ion is identified by intense doubly charged ion at m/e=414.																$(C_{12}F_9)_2(C_6F_5)P$
86*	976		parent ion is identified by intense doubly charged ion at m/e=488.																$(C_{12}F_9)_3P$
87	186		186	122	56	187	93	184	95	81	100	50	19	13	10	10	6	5	$(\pi-C_5H_5)_2Fe$
88*	334		identified by typical isotopic pattern of molecular ion																$(\pi-C_5H_4C_6F_4H)(\pi-C_5H_5)Fe$